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1925, VOL. 127, JUNE

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Chemistry at Interfaces.

A Lecture delivered before the Chemical Society on February 26th, 1925.

By Sir William Hardy, M.A., Sec. R.S.

When your Council invited me to deliver this lecture I was conscious more of the honour than of the responsibility. The sense of the former has not faded, but that of the latter has grown to terrifying dimensions. The fact of the matter is that I cannot hope to inform; the best I can do is to take this unique opportunity for propounding certain conundrums which have been forced on my notice during thirty years' work on interfaces and films.

The material I first worked with was proteins—or proteids as they were then called—and my studies led to a frankly chemical explanation of the properties of this singular group. In a physiological laboratory proteins, the physical basis of life, were still regarded as something outside chemistry and incapable of reactions of the ordinary type.

The protein class which attracted me was the globulins. They are singular in that, whilst themselves insoluble in water, they are dissolved as salts by acids, or alkalis, and, in the absence of acids and alkalis, by neutral salts such as sodium chloride. When dissolved by alkali, that is, when they react as acids, they form systems like soaps. Now the remarkable feature is this—I directed attention to it in the Croonian lecture for 1905—that the two types or states of solution, by acid or alkali, or by neutral salt, are discontinuous in the sense that to pass from one to the other the protein must first be precipitated, and that the protein masses are electrically charged in the first type of solution and are not electrically charged in the second type.

In that lecture I directed attention to the fact that while the electrically uncharged system in its phase relations can be homologated with such a straightforward system as that of water, sodium chloride, and succinonitrile, the electrically charged system, with contact potential differences at internal surfaces, manifests the abnormal viscosity, high degree of inertia to change, and other features characteristic of the colloidal state. The electrical aspect of this state has to my mind been too much neglected of late. I believed then, and I believe now, that colloid chemistry has much to gain from someone who will start from the rich literature of the Lippmann period. He, if anyone, may succeed in rescuing that much-abused word "colloid," and bringing it within the four corners of a satisfactory definition.

I tried myself—indeed I have tried many times—but it needed a better physicist than I am. The fundamental difficulty is easily stated. Take, for example, Dupré's equation for the free energy between two phases A and B

$$T_{AB} = T_A + T_B - 2T'_{AB},$$

the question is whether the final term, which gives the gain of work in forming the interface, can or cannot be divided into two which can be written

$$2T'_{AB} = 2T'_{ab} + f(\sigma),$$

when σ and $-\sigma$ are the densities of the electricity on either side of the interface.

$2T'_{ab}$ then is the work done by simple forces of cohesion, and $f(\sigma)$ the work done in forming the electrical layers. You may object at once that such a question is beside the mark, since all cohesive forces are now recognised as being electrical. I submit, however, that there is a real question. Contact potential implies a certain orderly disposition of the electric polarities and, on the chemical side, a corresponding orderly configuration of atoms and molecules with respect to the interface. Is all the free energy peculiar to the interface gathered in this orderly way, or is there a portion which does not directly contribute to the definite distribution of electricity which constitutes a contact potential difference? This question, to my mind, includes the question of the different valencies—co-valency, ionic valency, etc.

The first obvious step towards answering this question was to measure the potential difference between organic fluids and water and see what relation it had to chemical constitution. I made more than one attempt and obtained always an impossible result—namely, that the contact potential difference was almost independent of chemical constitution. The cause of failure is of interest. The only experimental method which suggested itself to me was to measure the movement of a small drop suspended in water in an electric field of known strength, but it seemed to be impossible to preserve so small an area of interface from contamination amidst such a relatively large mass of water.

Consideration of electrified internal surfaces does, at any rate, lead us directly to what I still cling to as the distinctive feature of colloidal solutions, namely, their inertia whereby a state is not defined simply by the temperature, pressure, and components, so far as they can be recognised, but also by the previous history. The path of approach has to be reckoned with. But although internal electrified surfaces give a high viscosity and a slow rate of change, they are not, I think, the whole story.

The theory of these salt globulins is simple. The insoluble protein is dissolved as a molecular compound with the neutral salt, in the same way that silver chloride is dissolved by sodium chloride. But it is rare to find a component in a solution in water which is so uncharged as to show no movement in an electric field. After much search, I found only one clear case—azomethine dissolved in chloroform—and here the fact is not evidence of the absence of a charge on the molecules of azomethine, because the electric flux necessary for electrophoresis was probably not possible.

Possibly there is no great physical interest at the moment in elucidating the molecular mechanism of contact potential—physicists seem satisfied with a simple electronic theory and chemists with a simple ionic theory—that of Nernst, but there is more to learn. What part do polar groups play? Where in the molecules oriented at an interface is the contact potential situated? And, above all, what are the conditions which permit of an electric flux?

The conditions of discharge of such contact fields are of peculiar interest to the biologist, and of basal importance in the study of that difficult subject the corrosion of metals.

Let me give an example which shows the need the biologist has for an intimate analysis of surface energy in terms of contact potential, of tension, and of orientation. The blood of lobsters and crabs flows, not in capillaries, but in large spaces called sinuses, spaces so large that, if one were freely opened, the animal would quickly bleed to death. These sinuses are torn open not infrequently in the misadventures of their lives. They fight, for example, and a great claw is often torn away in the conflict. Loss of blood on these occasions is reduced to a minimum by that natural first aid which serves us all, namely, the faculty of the blood when disturbed to clot. Clotting in this case must be swift, and it is surprisingly swift—the sinuses are plugged almost at once.

It is to the first stage in this process of clotting that I want to direct your attention. There are in that blood certain cells or blood corpuscles which have been called "explosive" cells, because on the slightest disturbance to the chemical or physical balance of the blood they actually do explode. The upset is due simply to contact of the blood with a "foreign body" which may be sea-water, or may be a glass slide. Using suitable precautions, one can get a drop of blood on to the under side of a cover glass and watch the process. By the time the microscope is adjusted the corpuscles nearest the glass have already exploded, but further down in the drop there are still intact cells and one can watch the progress of the disruption moving away from the glass face. A wave of change must start at the interface between the glass and the blood, and

progress through the latter, involving these sensitive corpuscles in its path. What is it at the interface which starts this wave of change? It has something to do with what might be called interfacial reactivity—that reactivity which lowers surface tension and increases the contact potential difference. So much we know because, if paraffin wax be substituted for glass, the change does not occur. I have long wanted to trace the effect of chemical constitution upon the phenomenon and have never yet had time. The change will start from a quartz face, but it must be remembered that it is unusually difficult to free a quartz face from a film of natural contamination.

The two impressive features of this phenomenon are (1) that a chemical change of catastrophic character can be started at an interface, and (2) that the change can be propagated apparently indefinitely through one of the phases.

You have all heard of nerves, nerve-fibres, and nervous impulses, which last are waves, partly electrical, which are carried by nerve-fibres. A nerve-fibre consists essentially of a fine rod of protoplasm from 2 to 8μ in diameter, and it is an outgrowth from a nerve-cell. These fine rods may attain a prodigious length—in a large animal like a whale, the rods which connect the cells in the spinal cord with some of the more remote parts of skin or muscle must be many yards in length, and each starts from a small object, the nerve-cell, which is only, say, 100μ in diameter. Now the structural integrity and capacity for growth—note especially the latter—of this tenuous filament depend throughout its length entirely upon its connexion with the nerve-cell of which it is an outgrowth, and the interface from which this control irradiates is without doubt that inside the cell between nucleus and cell body. There can be no question of mere gross manufacture and transference of nutriment—the process would require geological time. There must be some kind of static or dynamic balance just as a row of bricks up-ended on an inclined plane would fall if the support at the end were withdrawn.

So far as my limited knowledge goes, there is nothing in the inorganic world to parallel this dependence of structure, relatively or actually far distant, upon the integrity of a particular interface.

Let us form an interface say by bringing a paraffin, or one of the derived acids or alcohols, in contact with a solid face of glass or steel. There will be adhesion and we can now, from evidence derived from more than one source, be certain that the long molecules will be oriented at the solid face with their long axes at right angles to the interface. Does the effect of the interface end there? The forces involved are of very short range, less than any dimension

of the molecule. Their range is indeed of the order of the distances which separate the atoms in a molecule. But, if there is a monomolecular layer of oriented atoms formed at the interface, there will be a secondary interface formed between it and the mass of fluid where a random disposition of the molecules holds, and this will have its effect in orienting a second layer of molecules and so on. In fact, I picture the process going on until it is upset by the heat motions. The study of friction furnishes, I believe, proof that this limit set by the heat motions is not reached until several —one cannot say how many—layers of molecules are involved.

One has, therefore, at the interface a new phase—the interfacial phase, we might call it—which is formed with evolution of heat as Leslie pointed out as far back as 1802, in the formation of which, therefore, degrees of freedom are suppressed, and the phase has a configuration or structure which intrinsically is unstable at the given temperature and pressure, and acquires stability only by the intervention of the forces at the interface. Moreover, the phase is the seat of an electric field of prodigious intensity.

I accept the view that the forces at the actual interface—the adhesional forces of the solid—are, in fact, of exceedingly short range, because all those best qualified to judge are agreed as to this—but in some way they make themselves directly felt right through the interfacial phase so that the capacity for withstanding traction—the friction, in short—is never determined by the chemical nature of the lubricant alone, but by the chemical nature of the solid face as well. If it were merely a matter of setting a number of molecules of a given kind on end, layer on layer, the properties of any plane between the layers would depend merely on the particular kind of molecules bounding it. This never is the case—the physical properties of such a plane depend just as much upon the nature of the solids as upon the nature of the molecules.

Gibbs, it will be remembered, introduced with tremendous effect the conception of an interfacial phase, and what we are particularly concerned with is the depth of this phase. Leslie, more than a hundred years ago, pointed out that the intrinsic pressure—not the quantity p in Gibbs's equations, but the van der Waals pressure —is different in this phase from what it is in the body of the fluid contiguous to it.

The first evidence I will bring forward to support the statement that the interfacial phase may be many molecules in depth is final and convincing. Bragg and his fellow-workers have been analysing with the aid of X-rays the structure of thin layers of grease spread upon a solid face, and they find that the long paraffin molecules are oriented end-on to the interface, and that they are disposed in

rows one above another. There is, in fact, as I claimed many years ago, a kind of crystallisation at an interface with the crystal planes disposed tangentially.

There is one observation made by Bragg and his fellow-workers of peculiar interest to me. It will lead to a digression, but I hope an interesting one. They find that the grease when simply placed on the solid does not show this architecture, but develops it rapidly when rubbed or smeared upon the surface. This is, perhaps, what might be expected; the study of friction shows that orientation comes to its maximum slowly even when mobile fluids such as octyl alcohol, or caprylic acid, are used. With the latter, for example, friction falls, owing to gradually increasing orientation at the interface, for about 60 minutes at ordinary room temperature (11°). Such a period might be expected to be indefinitely long in a highly viscous grease.

It is really surprising how much mechanical agitation will shorten the period even when the lubricant has high fluidity. With caprylic acid on glass, orientation reaches a maximum, and friction reaches a steady value, when there is no mechanical disturbance, other than earth tremors, in about 60 minutes; but if the surface be disturbed by vigorously moving the slider about, it is completed in about 10 minutes.

It looks as though the first effect of the attraction field of the solid was to lock the molecules in the random disposition characteristic of the body of the fluid. Put in another way, the effect of the attraction field is to increase the viscosity of the fluid in the neighbourhood of the solid so that rearrangement under the influence of their polar or other attractions is delayed. There is direct evidence of such a change.

Mechanical agitation materially quickens the process of orientation even when the surfaces are covered only by an insensible film deposited from vapour. Consider this case for a moment. Caprylic acid consists of a carbon chain loaded at one end by the carboxyl group. The molecules might therefore roughly be likened to long rods the attraction of which for the solid face is greater at one end than at the other. These rods are, at any instant, disposed at random in the vapour, and therefore, when they move to the solid face, although an excess will strike with the more attracted end, say the carboxyl end, many will strike with the other end. The film as first formed will be far from completely oriented and there is a latent period or lag during which orientation becomes more orderly owing to the evaporation and condensation of molecules into and out of the vapour.

Left to itself, the film reaches a steady state, that is to say,

friction ceases to diminish, in about 10 minutes, but mechanical agitation, produced by motion of the slider about the plate, causes the steady state to be reached in a matter of seconds. Obviously in the second case something more than evaporation and condensation is at work—the molecules in the film must actually rearrange themselves on the spot, and the process of changing ends is hastened by mechanical agitation.

I could multiply instances, especially of the varying degree of sensitiveness to mechanical disturbance. I will take an extreme case, and the case reveals a paradox.

It is possible to deposit films in succession upon a solid face, and friction values reveal that they actually are in succession. The stability of the arrangement obviously depends upon the order in which the films lie. For example, a clean surface of glass or steel can be covered with an insensible film of solid paraffin, or oleic acid, or undecyl alcohol, or undecoic acid, etc., and a second film of water deposited on this film by admitting water vapour. With great care to avoid mechanical agitation, the friction of the doubled film can be observed, but the disposition is highly unstable if the first deposited film is fluid, and almost any degree of movement upsets it with consequent change of friction. Here are the figures for undecyl alcohol:

Alcohol alone.	Water vapour admitted.	Mechanical agitation at once rose to
$\mu = 0{\cdot}44$	$\mu = 0{\cdot}33$	$\mu = 0{\cdot}48$

I see in this an interesting possibility. Let us suppose there is a righting mechanism which, by expenditure of energy, would, given the opportunity, restore the original disposition of the films. I am, of course, thinking of living matter. Such layered films might reach any degree of sensitiveness to mechanical shock, and you obviously have here the germ of the mechanism of a sense-organ capable of reacting to any kind of mechanical disturbance. More than that, by having a succession of films rightly arranged one could get an effect magnified, and it is at any rate noteworthy that in what are believed to be organs of the pressure sense—of traction at any rate—one does get a succession of surfaces about a nerve-ending, like the coat of an onion.

Here we see the importance of not losing sight of the contact difference of potential. These films, no matter how thin, are at a different potential from that of the substance on which they lie. I was able to observe this as far back as 1911; and the fact is, of course, the basis of frictional electricity as Helmholtz recognised, although he did not specify or, I think, visualise an actual film of foreign matter. Any disturbance of the films, whether single or

doubled, is certain, therefore, to produce a redistribution of electricity; so the way for an effect on the end of a nerve fibre is clear.

To complete the story—the possibility of producing a succession of films depends upon the immiscibility of the first-used substance with water. When the substance is miscible with water, unstable states are not produced and water vapour always and at once increases friction.

Benzene vapour, on the contrary, when used in the same way always lowers friction.

Let me pick up the paradox before I forget it. Water is, it will have been noticed, a lubricant in these cases. This is obvious when a plate of solid paraffin is used. Here is a table of values of great interest:

Glass lubricated with tetracosane:	$\mu = 0{\cdot}325$.
Water film formed on the composite surface:	$\mu = 0{\cdot}110$.
Tetracosane on tetracosane:	$\mu = 0{\cdot}060$.
Water film deposited on solid tetracosane from vapour:	$\mu = 0{\cdot}025$.

But water is entirely without lubricating action on clean glass, steel, bronze, quartz, or bismuth. I do not want to be mistaken here. Water, of course, can act as a lubricant in the hydrodynamical sense investigated by Osborne Reynolds. That is to say, if the solids are kept apart by a pad of water held in place by external forces, it has the lubricating properties of a fluid with its physical characters. But in the boundary region, a film of water, or a pool of water, has no power of lowering the friction between these various solids. Yet it can alter the state of the surface of a substance so, in a sense, inimical to itself as a normal paraffin, and reduce the friction by more than 40 per cent. This peculiar feature of water, the limitation of its powers as a lubricant, is at present wholly without explanation.

Water in a sense is an abrasive. It decreases to a startling extent the lubricating powers of all substances with which it is miscible in the boundary zone. A trace of water will destroy the lubricating power of one of the lower alcohols. In this sense, water is a true abrasive, although it has no influence one way or the other on the friction of clean faces.

Glycerol is another of these neutral substances, although owing to its high viscosity it is not easy to get rid of the flotation action. However, if surfaces are forced together through the pad of glycerol, disaster quickly follows. A case was brought to me a few days since of ball bearings, lubricated only with glycerol, in which the balls were quickly torn into fragments. A chemist would, I believe, expect glycerol to behave like water in most respects.

A short while back I postulated a righting moment which should restore a film which had been destroyed. Here is an example

which is remarkable, because the righting moment is exerted at a distance and depends for its operation upon the integrity of another interface.

Eggs of certain starfish, because they are large, have been much studied by the methods of microdissection. A thin film can be detected under the microscope covering the surface of one of these eggs. When this film is pierced and the contents of the egg, the living substance, are injured over a limited area, repair is effected by the re-formation of this surface membrane between the injured and uninjured parts. This is the process of healing. The injured parts are beyond repair and they are simply cut off by this membrane formation. There is here that righting power which I postulated.

But the righting power depends, as in the example given earlier, upon the intactness of the interface between nucleus and cell-body, for if the fine needle is simply pushed into the cell until it punctures the nucleus of the egg, the superficial film, instead of being reformed, perishes over the whole body of the cell and in a curious fashion, for it disappears first about the point of entry of the needle, and then the solution or disappearance progresses slowly over the whole surface. Following on this, the whole cell becomes invaded by water and breaks up.

One must suppose that the influence of the nucleus or the nuclear interface must diminish with distance—the righting power will diminish—and this I cannot but suppose is one of the factors which sets a limit to the size of the living cell.

I will now return from this somewhat long digression to the question of the depth of an interfacial phase and consider it in the light of measurements of friction.

It will be necessary first briefly to summarise the evidence. Consider a flat plate covered with fluid and a heavy body falling under its own weight through the fluid. As it falls it must displace the fluid lying between its lower surface and the plate. The time occupied in falling will, therefore, be a function of the viscosity of the fluid, the area of the plate, the distance through which it falls and, to a remarkable extent, the shape of the surface of the falling body. The equations for the time occupied in falling, which have been worked out by Professor G. I. Taylor, show that whilst the time needed to fall completely through the fluid to the plate is always infinite, the infinity is of a low order if the under surface of the falling body is curved, and of a high order if it is plane.

Calculated with the help of these equations, the time needed to fall through water to a molecular distance from the plate is a matter of hours for a plane slider—as I will call the falling body—and of seconds for a curved slider.

As the layer of lubricant between the faces is thinned by the fall of the slider, one may expect the friction to increase; therefore, by following the changes in friction after the slider has been put in a pool of lubricant, one can follow its fall. There is, in short, a lag or latent period following the placing of the slider in the pool whilst the former is falling through the fluid.

Now when the slider is plane this lag actually lasts for an hour or more, but when it is spherical it is so short as to be indetectable. It must be remembered, however, that it takes 20 seconds to make a measurement of friction.

Before giving actual figures, I must, to avoid misunderstanding, point out that a lag or latent period before a steady state is reached can be due to one or both of two things—to the time occupied in falling through the lubricant, or to the time occupied in the orientation of the molecules of the lubricant with respect to the normal to the surface of the plate. Time does not permit me to give the evidence in detail. It must suffice to say that when paraffins or their derived acids or alcohols are used, lag due to orientation is exhibited only by the latter two classes, in which the two ends of the elongated molecules differ. No lag due to orientation has been detected with certainty when the lubricant is a normal paraffin.

There is another way to discriminate between the two causes. When the lag is due to orientation, friction diminishes during the latent period, but when it is due to thinning of the layer of lubricant friction increases during the latent period.

Here is an example of a latent period of increasing friction due to fall of the slider through the lubricant.

Undecane.

	Pull in grams.	μ.		Pull in grams.	μ.
1 sec.	3·06	0·15 (approx.)	30 mins.	10·98	0·538
5 secs.	6·53	0·32 („)	45 „	11·14	0·546
1 min.	8·77	0·43 („)	60 „	11·14	0·546
5 mins.	9·85	0·483	90 „	11·20	0·549
10 „	10·57	0·517	120 „	11·20	0·549
15 „	10·83	0·531	180 „	11·20	0·549

What is the steady state? Is it a state in which the layer of lubricant has reached a constant value? In other words, has the slider ceased to fall because a layer of definite thickness and of great mechanical stability has been reached? Apparently not, because if additional weight is placed on the slider there is a further rise in friction and another latent period of rising friction which ushers in a new steady state. Similarly, if the weight is reduced there is a latent period of falling friction. In short, the slider

appears to move up or down the fluid according as the load is decreased or increased.

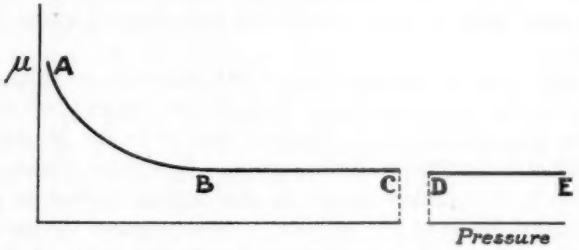
Plane slider of steel, lubricated with a large excess of liquid nonadecane. Latent period measured for increase in weight of slider.

Initial load (g.).	Original μ. (Steady value.)	Weight added (g.).	μ After adding weight. (Steady value.)	Latent period (mins.).
120·4	0·2523	50	0·2441	12
420·4	0·2105	50	0·2055	5
821·2	0·1871	50	0·1857	± 1

This process, however, has a limit, for when the load is high enough variations of load are not followed by a latent period.

These various features are best exhibited by a curve (Fig. 1) in which the coefficient of friction, μ = friction/load, is plotted against the pressure between the bearing faces or load/area.

FIG. 1.



You will notice over the first part of the curve μ is falling. Now this is itself remarkable, for μ is a measure of the efficiency of a lubricant with respect to a single variable, the load. Over this part, AB, there is the latent period characteristic of variations in the depth of the layer of lubricant owing to the slider rising or falling in the fluid. We have, therefore, the curious fact that the efficiency of a lubricant increases as the layer thins until it reaches a maximum at B.

At B over the horizontal part, there is no latent period of the kind mentioned. If any point in BCDE is taken and the load varied, but not enough to trespass on the region AB, the adjustment of the load to the friction is sensibly instantaneous.

There is a fundamental and surprising law of friction, which was formulated by Amontons in 1699, according to which the friction is equal to the load multiplied by a parameter which of course then is the coefficient of friction, μ. This law holds rigidly over BCDE and does not hold over AB.

The part DE refers to a spherical slider. It is obvious that

from its shape the pressure under a spherical slider must be immense, and to indicate this I have broken the scale of pressure. A spherical slider owing to its shape at once cuts right through the lubricant until the limiting layer characteristic of the whole region BCDE is reached, and this alone would explain the fact that one never gets any indication of rising or falling of a spherical slider in the lubricant.

It is not my business here to discuss this curve in detail, that will be done elsewhere. It will suffice if I say that over the region AB the layer of lubricant would appear to be many molecules thick, and that there the adjustment of friction to the load is effected by an actual flowing in and out of lubricant from between the surfaces of slider and plate, whilst over the region BCDE this process ceases and the adjustment of friction to variation in the load is by the elastic forces between the atoms, and for this reason it occurs with a rapidity too great to be detected. It is only when interatomic forces alone are concerned that Amontons's law holds.

I can now take up the question of spreading of effect from the interface.

At A the layer of lubricant is several molecules in thickness, yet the state is far removed from that of the interior of the fluid. The layer can exhibit static friction, that is to say, it can carry a stress without continuous deformation. Somehow, throughout its entire depth, the molecules are to this extent locked in place by the attraction fields of the solids. It is structured throughout and the maintenance of the structure is due to the fields of the solid.

It is legitimate to assume that the plane of slip is midway between the solid faces. If the state of the lubricant were unchanged there, the friction would be independent of the nature of the solid and be a function only of the constant which defined the state of the fluid. This is not so—the same lubricant at the point A in the curve gives entirely different values of friction for different solids. The following table illustrates this:

Steel slider. Face plane. Load 20·4 g., corresponding to point A on Pressure/μ curve. Lubricant octyl alcohol.

Plate.	μ.
Medium carbon steel	0·463
Mild carbon steel	0·457
Nickel chrome steel	0·469
Phosphor-bronze	0·510
Bismuth	0·438
Glass	0·523
Quartz	0·472

I do not want to press this evidence too far, because the experimental conditions were not rigidly controlled, but, under conditions

in which there would appear to have been a layer of water several molecules in thickness between the faces, we find water:

antilubricant	for	glass	on wood
lubricant	,,	,,	,, ebonite
neutral	,,	,,	,, sulphur
	,,	,,	,, glass
	,,	,,	,, steel
	,,	steel	,, steel.

The physical properties of water, which depend upon its molecular structure, are changed by the force-field of the solid and the change penetrates some distance into the fluid.

Further experiments—measurements in the region AB with different solids—will, I hope, enable us to formulate what might be called the law of transmission, that is, the variation in the effect of the field of the solid with distance along the normal. That has been done only in the region DE and to the results I will now turn.

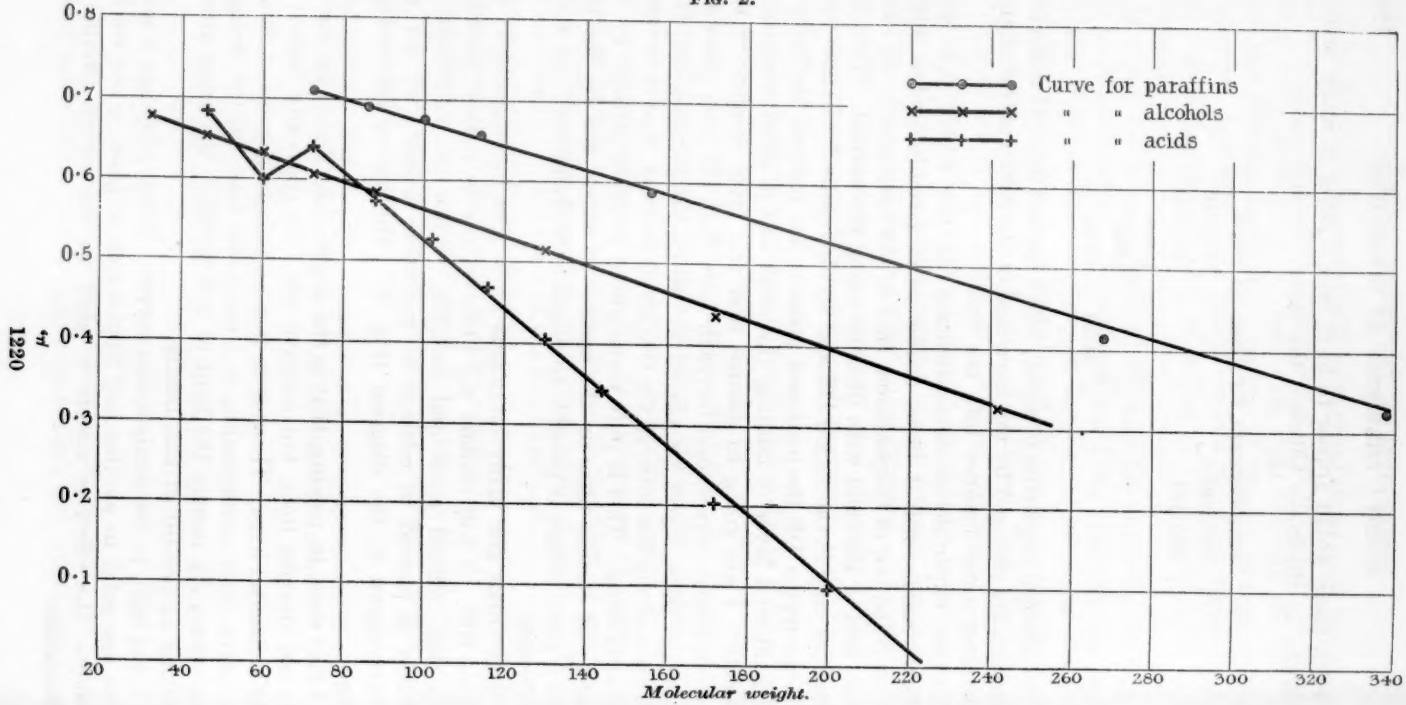
In the region DE the increased pressure has reduced the layer of lubricant to a layer of limiting thickness and of great mechanical stability. I am going to assume that this layer consists of two monomolecular layers, one for each face, that the long molecules in each of these layers are placed on end on the surfaces, and that the plane of slip lies between the two layers midway, that is, between the solid faces. This is pure assumption, justified perhaps by the analogy of certain films on the surface of water, and by the fact that it alone makes it possible to visualise the relations I am about to describe.

Many solids and many lubricants have been investigated in the region DE. I will confine my observations to normal paraffins and their related acids and alcohols. When the coefficient of friction is plotted in relation to molecular weight, we get the curves shown in the diagram (Fig. 2). The curves are straight lines.

I may note, in passing, that in the region AB (Fig. 1) the curves are not straight lines, but concave with the convexity turned to the horizontal axis. There is in fact an infinite number, a family of curves, each corresponding to a particular load and the straight-line curves are merely the limit of this family. We know almost nothing at present of this family.

Going back to the straight-line curves. When a change is made from one solid to another, say from a steel to glass, or one steel to another, the effect is merely to shift all the curves parallel to themselves.

FIG. 2.


0·8
0·7
0·6
0·5
0·4
0·3
0·2
0·1
μ
1220
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300
320
340
Molecular weight.
Curve for paraffins
" " alcohols
" " acids

The equation for the curves therefore is

$$\mu = b - aM,$$

where b is a parameter depending upon the chemical nature of the solids and a only upon the chemical series, paraffin, acid or alcohol, as the case may be.

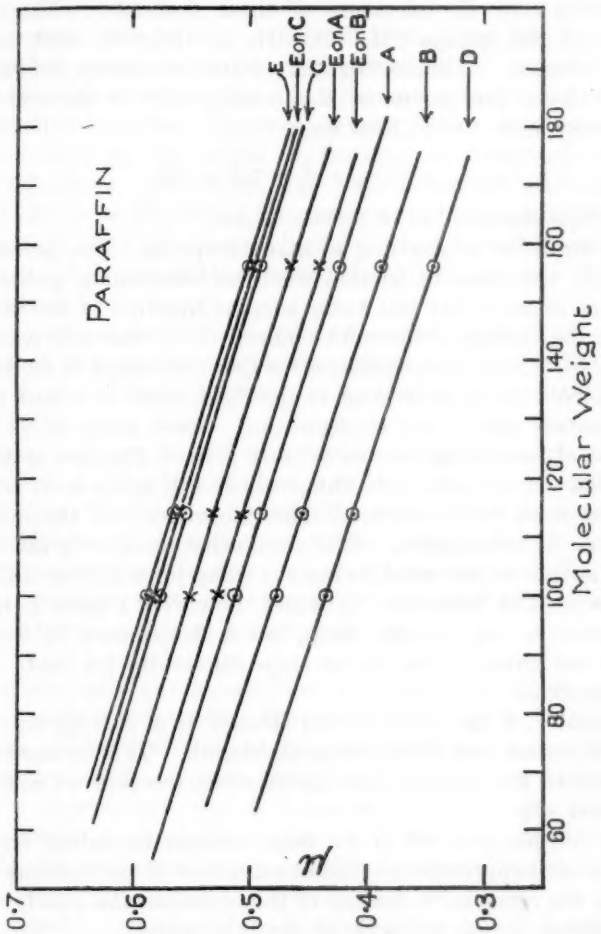


FIG. 2.

If two different solids are used, if the slider, for example, is of bronze and the plate of steel, each solid produces its effect independently of the other, so that the equation becomes

$$\mu = \tfrac{1}{2}(b_1 + b_2) - aM,$$

where 1 and 2 refer to the two solids.

Now, when the curves for a number of solids were compared a relation was disclosed which was satisfied by the equation

$$\mu = b_0 - d - aM,$$

in which b_0 depends only upon the solid, d only on the chemical series, and a is as before.

Consider now the structure of these molecules. They consist always of end groups CH_3, $CO{\cdot}OH$, or $CH_2{\cdot}OH$, with a carbon chain between. Eliminating aM, which obviously refers to the carbon chain, the parameter d can refer only to the end groups, so we may write as the final form

$$\mu = b_0 - d - c(N - 2),$$

where N is the number of carbon atoms.

This equation is startling in many respects. The parameter b_0 is merely the value of friction when no lubricant is present.

Let us assume that this value is some function of the attraction field at the surface of the solid—indeed this is the only assumption open to us—then the equation means that each atom of the lubricant is responsible for a decrement in this field which is a pure function of its nature and of the configuration. Each atom is, as it were, capable of saturating or neutralising a fixed fraction of the field.

I want you to notice one thing which will mean more to you as chemists than it does to me. The parameter c is the decrement due to each carbon atom. It is a quantity completely independent of the nature of the solid, being the same for solids so different as glass, steel, and bismuth. It is not, however, a fixed property of the carbon in the paraffin chain, but is determined by the nature of the end group. The curves slope differently for acids, alcohols and paraffins.

Obviously, if the chain is long enough, if N is large enough, the field will vanish and there will be no friction. This we have actually observed to this extent, that the smallest traction we could apply produced slip.

Let this happen—let N be large enough to reduce friction to zero—what happens to the field of attraction of the molecules itself? That is the remarkable feature of the equation, the purely negative part played by the molecule of the lubricant.

I raised the question quite early in this lecture, whether all the work done by the cohesive forces other than that dissipated as heat was expended in setting up the contact potential difference. Here is an indication, no more, that it is not.

Friction when the limiting layer alone is involved is, as we have just seen, a linear function of the molecular weight; but the capacity

for reducing the contact potential between water and mercury emphatically is not, as Guyot's measurements show. Like the total work of adhesion to mercury, the capacity for reducing the contact potential increases as the carbon chain lengthens, but not in proportion to the lengthening.

We may suppose that b_0, the friction of clean unlubricated faces, is some function of the cohesion field on the face of the solid, and the equation given above then tells us that this field is gradually extinguished as the carbon chains lengthen.

The cohesion between these paraffin substances and the solid faces should therefore increase as the chain lengthens. The cohesion—that is, the work of forming an interface—between these substances and water has been measured and found to depend almost wholly upon the end groups. It is independent of the length of the chain in the alcohols and acids and increases only slightly in the case of the paraffins (*e.g.*, C_6, 19·99; C_{10}, 24·12 dynes per sq. cm.).

But, according to Harkins, with the metal mercury the work of cohesion at the interface increases greatly with the length of the chain (*e.g.*, paraffins, $\pm$ 5 dynes per *carbon*; alcohols, $\pm$ 10 dynes per *carbon*).

There is a simple way of showing the effect of a lubricating film upon cohesion. A plate of glass is cleaned, lubricated with a film of insensible thickness, and roughly cleaned as to one-half by passing the flame of a Bunsen burner quickly across it. Clean mercury is now finely sprayed on to the surface, and the plate is then turned upside down; the drops of mercury fall off the lubricated part and remain cohering to the clean part.

Something may be gleaned from the properties of free films as to the distance through which the state at any interface may extend.

It was, I believe, Gibbs who first suggested that a soap film consisted of two walls or skins with fluid between. In Reinold and Rucker's papers each wall is taken to be merely the superficial parts wherein surface effects are resident—the depth of each "wall," therefore, was equal to the "range" of the cohesive force.

It is, however, quite easy to construct a film in which the surface wall is without doubt a chemically distinct structure. If a film of, say, oleic acid be formed upon clean water, the density of the film being less than that required to produce the full fall of tension, and a ring of, say, copper wire—that is what I used in my experiments—be gently withdrawn from the body of the water, a film is formed over the ring which is of astonishing stability if the

right concentration of the oleic acid on the surface has been hit off. I have passed such a film in lecture round a big class without its breaking.

There can be no doubt here as to the structure of the film. The composite surface has merely been folded together so that there are two skins of oleic acid, AA′ in the diagram (Fig. 3); one on each surface with a plate, B, of water between them. By observing the motion of particles under the microscope when a weak electric field is established in the film, it is possible to convince oneself that the skins AA′ are at a different potential from the water between them. The skins of oleic acid are always negative to the water.

Many years ago—in 1885—Reinold and Rücker described how the passage of a small current through a soap film would prevent it thinning under the action of gravity. The difference of potential between surface skins and middle plate noted above accounts for this. When one watches such a process under the microscope one sees that the superficial skins show no movement at all, they seem quite rigid, but the internal plate of fluid flows under the influence of the electric field.

Now, if the internal plate of fluid were merely fluid as in mass and unaffected by the interfaces on either side of it, the tension of the film and its specific electric conductivity would be independent of the thickness. This, indeed, is true of a soap film until it thins to about 50 $\mu\mu$, when, as you all know, tension becomes a rapidly varying function of the thickness. If x is the thickness, the sign of the quantity dT/dx changes from negative to positive, and remains so until the thickness falls to that of the black film, which is about 11 $\mu\mu$.

Reinold and Rücker, following a suggestion made by Clerk Maxwell, attributed this change to instability—because the film obviously is unstable when the coefficient is positive—to a change in the force of cohesion from an attraction to a repulsion. They supposed that the force was a repulsion from 50 to 11 $\mu\mu$ and then again became an attraction.

No one I suppose holds that view now. The accepted theory of the stability of free films is based upon the variation of superficial tension of water on whose surface is spread some "active" substance, that is, some substance which lowers the tension. If a free film thins under its own weight for example, the concentration of active substance on its surface diminishes and the tension rises. So long as this happens, the film is stable.

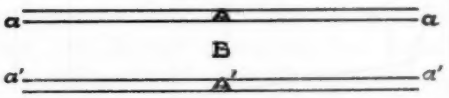
This theory, however, fails to account for the curious instability over certain variations of the total thickness, because in my opinion it concentrates attention on the surface films to the neglect of the

middle plate: yet the microscope shows that it is in the middle plate where adjustment is made to imposed stress.

McBain and Jordan Lloyd, using the ultra-microscope, have shown that the colloidal particles in a solution of soap or gelatin become attached to one another to form threads. In certain solutions of protein, the growth of such threads can be followed with the ordinary microscope, and they are seen to become attached to one another so as to form a framework or sponge.

In a stretched structure such as a soap film the direction of such threads with respect to the tangent will be determined by the lines of stress. I was able to observe this in protein solutions. Let them be disposed in the middle layer, B (Fig. 3), at right angles to the surface with their ends anchored in the interfaces *aa*, *a'a'*. When the middle layer thins so that the threads can stretch completely across from *aa* to *a'a'*, a critical point in the history of the film will be reached, for it is known that such threads tend to shorten—

FIG. 3.



the property of shrinkage, or "synaeresis" as Graham called it, of jellies depends upon this property—and drainage of free fluid from the film will be hastened. If this occurred more rapidly at any point than elsewhere, the tension at that point would fall, and rupture would occur were it not for the stiffening due to the framework.

A soap film is symmetrical in the sense that the films A, A' on each face are the same. When they are not similar, other phenomena appear.

It is easy to make an unsymmetrical film by liberating a bubble of air under water which is covered by a skin of some substance such as oleic acid which is immiscible with it. If the water be chemically pure and freed as far as possible from active substances by scraping its surface, the amount of contamination available for forming a skin on the inner face of the bubble will be very small, and the time available for condensation at the face very short, namely, the time occupied by the bubble in rising through a centimetre or so of water. The density of the skin on the upper surface of the water is under the control of the experimenter and may be varied as desired.

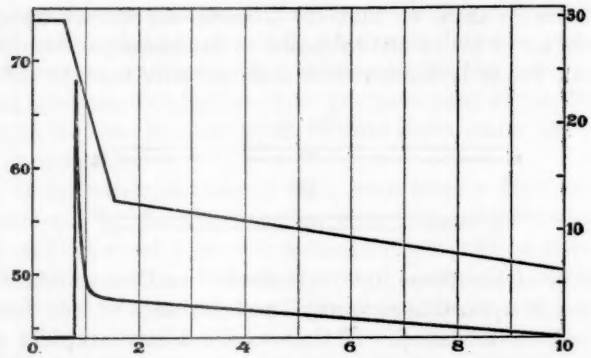
When the bubble has risen to float on the surface, the free film therefore has an exceeding small amount of matter condensed on

its lower surface and can have any density of a known component the operator may desire on its upper surface.

The mechanical stability can be gauged from the time the bubble lasts on the surface. During this period the film will be thinning by drainage of the water in the middle plate, B, and the apex obviously will thin most rapidly. The bubble bursts when, owing to the thinning, the tension begins to fall at the apex.

Now one finds that the duration of the bubbles, that is, the amount of drainage they can stand before they become unstable and burst, is a remarkable function of the tension of the composite surface oleic acid–water, that is, of the density of the acid on the water face.

FIG. 4.



The scale of tension of the general surface of the water is given on the left, and the upper curve is the curve of tension. The time scale in seconds is given on the right, and the lower curve gives the duration of the bubbles. The abscissæ give the calculated thickness of the layer of oleic acid on the surface of the water in μμ.

Here is the curve, with the curve of tension also (Fig. 4). You will notice that there are two points at which the bubbles have no stability, that is to say, when they burst at once and with a peculiar, sharp click. The first is the region in which the tension is that of pure water, and the second is that in which the surface of the water is saturated or rather oversaturated with oleic acid. (Other substances give the same result.) But the most striking thing is that one passes from extreme instability to maximum stability at once. There is, in fact, a discontinuity of state.

Why should stability decline as tension falls? The variation of tension with the concentration of oleic acid cannot be the cause, because the curve relating them appears to be a straight line. In other words, dT/dF = constant.

I suggest that the mechanical stability of the film falls as it becomes less symmetrical owing to the increasing difference

in the density of A and A′ (Fig. 3). The amount of contamination on the inner face (A′) must be exceedingly small and therefore the two surfaces of the film are most nearly alike in state when the contamination, say oleic acid, on the upper surface, A, is also small in amount.

The water in B is, in short, modified throughout by the interfaces *aa*, *a′a′*, and when those interfaces are not similar it is like an unannealed plate.

Another instance of the influence of the forces at an interface extending through a layer of fluid many molecules thick is found in the way liquid will cause a ball to stick in a cylindrical hole when it has a clearance of 0·0001 inch. This case is discussed by A. A. Griffith (*Phil. Trans.*, 1920, *A*, **221**, 196), who supposes that the ball is bound to the inner surface of the cylinder by chains of molecules stretching from interface to interface.

A last word as to why a biologist, in spite of the handicap of his imperfect training for the task, is justified in sticking so obstinately to this problem of the distance to which the matter on either side is modified by the field of force at the interface. It is because it offers a slight and precarious but definite foothold in the most obscure region of biology. Growth, and its fellow repair, considered as physical processes are almost wholly beyond existing knowledge. The fidelity with which structure repeats itself is obvious in heredity.

Recent work, if anything, deepens the mystery of living matter, of how it preserves its space pattern, how it can be the *milieu* of chemical processes of peculiar and special kind, how it can maintain within itself sinks and sources of energy. It contains it is true a multitude of suspended particles, but these seem to be merely enclosures. When they are driven to one side, as they can be by centrifuging, the material is an optical vacuum. Take the nucleus —what is it?—apparently no more than a pellicle or skin, a mere bladder containing fluid!

CLXVII.—*The Ionisation of Aromatic Nitro-compounds in Liquid Ammonia. Part I.*

By (Miss) MARGARET JOYCE FIELD, WILLIAM EDWARD GARNER, and CHRISTOPHER CAIGER SMITH.

ORGANIC nitrogen compounds undergoing ionisation in liquid ammonia may be classified into three main groups: (1) amides and imides the conductivity of which arises from their behaviour as "ammono-acids," (2) aliphatic nitro-compounds which conduct

through the production of ammonium salts of pseudo-acids, and (3) aromatic nitro-compounds the mode of ionisation of which is yet uncertain. Of the last class, Kraus and Franklin (*Amer. Chem. J.*, 1900, **23**, 277; *J. Amer. Chem. Soc.*, 1905, **27**, 197; *Z. physikal. Chem.*, 1909, **69**, 272) have studied a number of mono-, di-, and tri-nitro-derivatives and the results they obtained with *o*-, *m*-, and *p*-dinitrobenzene have indicated that the conductivities in liquid ammonia are very sensitive to changes in the position of the nitro-group in the benzene ring. Thus the conductivities of solutions of *m*-dinitrobenzene were comparable in magnitude with those of typical salts in ammonia, whereas *o*- and *p*-dinitrobenzenes were comparatively feebly ionised in solution.

These authors have not, however, considered the mechanism of the ionisation of this class of nitro-compounds.

If the ionisation of aromatic nitro-compounds, as in the corresponding aliphatic substances, occurs through the formation of an ammonium salt of a pseudo-acid, then, on electrolysis of a solution in liquid ammonia, organic ions would be discharged at the anode and ammonium ions at the cathode with the liberation of hydrogen gas. The direction of movement of the organic ions of *m*-dinitrobenzene in an electrical field is in agreement with this view, but since electrolysis is not accompanied by the liberation of hydrogen at the cathode and as the hydrogen is not used up to any marked extent in reducing the nitro-compound, it can be definitely stated that the ionisation does not occur through the formation of the ammonium salt of a pseudo-acid. Also, since the cathode solution after the electrolysis is colourless, consisting solely of anhydrous ammonia with a high resistance, it appears that the ionisation of *m*-dinitro-derivatives is of an unusual type.

The kation is very probably an ammonia molecule carrying one or possibly two positive charges. The ionisation may thus be analogous to that discovered by Kraus for solutions of sodium in liquid ammonia, which occurs according to the equation $Na + xNH_3 \longrightarrow Na^+ + xNH_3^-$, a negatively-charged ammonia ion being produced. It is suggested that in the case of the *m*-dinitro-derivatives the ionisation occurs according to an equation of the type

$$(1)\quad R(NO_2)_2 + xNH_3 \rightleftharpoons R(NO_2)_2,xNH_3 \rightleftharpoons R(NO_2^{--})_2 + xNH_3^+,$$

the values of x and the magnitude of the charges on the anion and kation being for the present unknown. On electrolysis, the colourless ammonia ion travels to the cathode, is discharged, and becomes an ordinary solvent molecule.

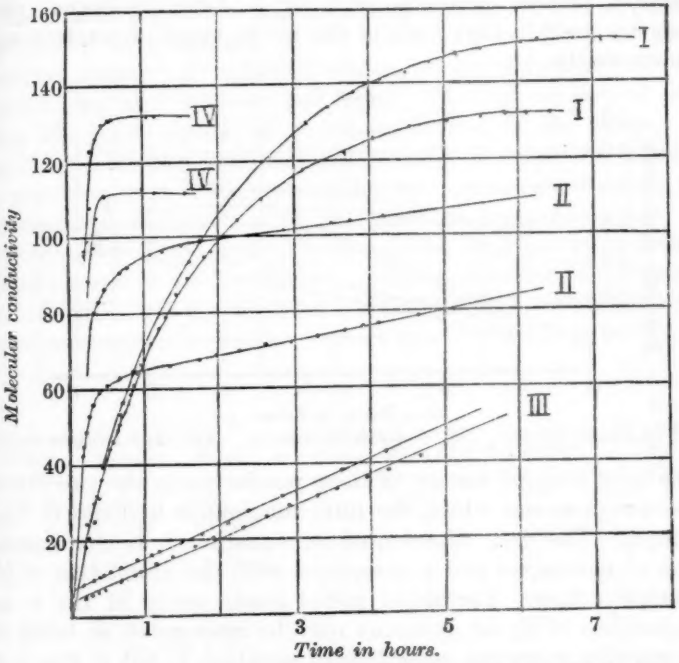
In many respects, the above two types of ionisation are analogous to those occurring in cataphoresis experiments with colloids, and

it is not impossible that the anion of the nitro-compound may be a colloidal particle with high mobility. In any case, its constitution is of considerable interest. The following is suggested as a possible mechanism for the ionisation

$$R{-}N\begin{matrix}O\\|\\O\end{matrix} + 2e = R{-}N\begin{matrix}\bar{O}\\|\\\bar{O}\end{matrix},$$

the nitro-group acquiring two negative charges.

FIG. 1.

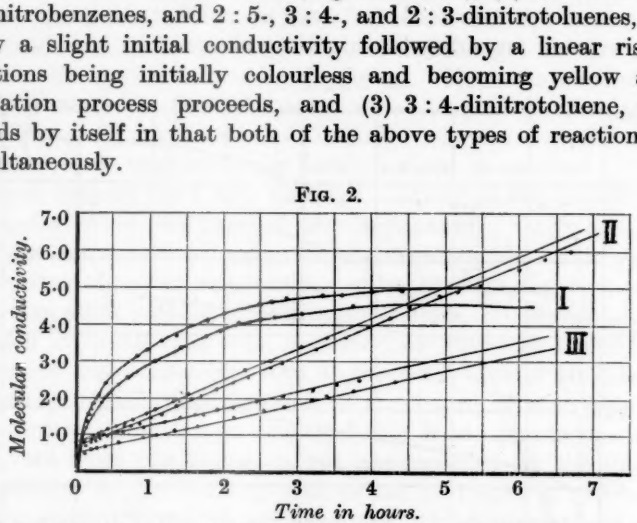


I. 2:4-*Dinitrotoluene.* II. 3:5-*Dinitrotoluene.* III. 2:5-*Dinitrotoluene* IV. *Dinitrobenzene. At dilutions* $V = 416{\cdot}2$ *and* $208{\cdot}1$ *litres.*

It was intended to study the dissociation constants of the complete series of isomeric nitro-benzenes and -toluenes with a view to test this hypothesis, but this was found impossible on account of the slow changes in conductivity which occurred on making up the solutions and after each dilution with fresh ammonia. As this change appeared to be associated with the formation and ionisation of an addition compound with ammonia, it was probable that measurements of the rate of change would throw light, not only on the mode of ionisation, but also on the differences between the constitutions of the isomeric dinitrobenzenes. The velocity of

the ionisation process was therefore followed by conductivity measurements. The curves obtained fall into three main groups: (1) those of *m*-dinitrobenzene, and 2 : 4- and 2 : 6-dinitrotoluenes, which start from zero conductivity and rise to an equilibrium value with a velocity indicating that the ionisation process follows a monomolecular law (Figs. 1 and 2), (2) those of *o*- and *p*-dinitrobenzenes, and 2 : 5-, 3 : 4-, and 2 : 3-dinitrotoluenes, which show a slight initial conductivity followed by a linear rise, the solutions being initially colourless and becoming yellow as the ionisation process proceeds, and (3) 3 : 4-dinitrotoluene, which stands by itself in that both of the above types of reaction occur simultaneously.

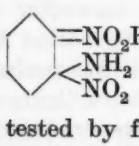
FIG. 2.



I. 2 : 6-*Dinitrotoluene.* II. 3 : 4-*Dinitrotoluene.* III. 2 : 3-*Dinitrotoluene.*

The most striking feature of these results lies in the two distinct ionisation processes which the nitro-compounds undergo in liquid ammonia. The first, represented by equation 1, is characteristic of the *m*-derivatives and is associated with the production of blue or purple colour. The slight initial conductivity of the *o*- and *p*-derivatives in liquid ammonia may be interpreted as being due to a reaction occurring according to equation 1, but if this is the case the intermediate compound must be colourless or present in extremely minute amount.

The second type of ionisation process takes place very slowly with a linear rise in conductivity and is shown mainly by the *o*- and *p*-derivatives. The production of a yellow colour during this change is an indication of the formation of a pseudo-acid with a quinonoid structure, perhaps in the manner

(2) 

postulated by Kenner and Burton (J., 1920, **117**, 852) with the formation of substances of the annexed type. This view, however, requires to be tested by further investigation. Both reactions (1) and (2) occur simultaneously in the case of 3 : 5-dinitrotoluene.

The maximum conductivities due to reaction 1 (Table I) may be regarded as a measure of the degree of ionisation of the nitro-groups and hence of their electronegative character. They have a bearing, therefore, on the problem of the influence of substituents in the benzene ring on the negativity of the nitro-group. The deductions which can be made from the results in this respect are (*a*) that the nitro-group in a *m*-position strongly increases the electronegative character of a nitro-group, and (*b*) that the methyl group increases the negative character of the nitro-group when in the *o*- and *p*-position and decreases it when in the *m*-position. The degree of ionisation of the *m*-derivatives decreases in the following order: 2 : 4-dinitrotoluene, *m*-dinitrobenzene, 3 : 5-dinitrotoluene, and 2 : 6-dinitrotoluene. The last is out of place, being the least instead of the most ionised of the series. The departure from the predicted order could, however, be explained on grounds of steric hindrance by the methyl group, but until the chemical composition of the addition compounds has been investigated it is not profitable to consider such points in detail.

The nature of the parallelism existing between the maximum conductivities and the heats of formation * and melting points of the nitro-compounds will be evident from Table I.

TABLE I.

Nitro-compound.	Colour in liq. ammonia. Initial.	Final.	Max. mol. cond. due to reaction (1). $V=208{\cdot}1$.	$V=416{\cdot}2$.	$\Delta\mu$ per hr. Reaction (2).	M. p.	Heat of formn. Kg.-cal./gm.-mol.
2 : 4-D.N.T.	Blue	Blue	133	152	0·00	70·5°	+12·2
3 : 5- ,,	Purple	Purple	62	91·5	3·7	92·8	+12·0
2 : 6- ,,	,,	,,	4·5	4·9	0·00	64·3	+10·7
2 : 5- ,,	Colourless	Yellow	3·5	6·5	8·5	51·2	+ 9·8
2 : 3- ,,	,,	,,	0·45	0·7	0·45	59·6	+ 5·4
3 : 4- ,,	,,	,,	0·5	0·7	0·85	58·9	+ 5·1
m-D.N.B.	Blue	Purple	112	132	0·00	90·0	+ 3·0
p- ,,	Colourless	Yellow	0·3	0·75	0·8	171·0	+ 9·9
o- ,,	,,	,,	0·5	1·2	1·0	116·5	− 0·2

EXPERIMENTAL.

Electrolysis of m-*Dinitrobenzene in Liquid Ammonia.*

Materials.—Commercial anhydrous ammonia (99·95%) was employed in the preliminary measurements, and ammonia dried over sodium in the final ones. A quantity of commercial *m*-dinitrobenzene (m. p. 83°) was crystallised four times from alcohol and then melted at 89°. This specimen was used throughout the experiments.

Solubility.—The solubility of *m*-dinitrobenzene in liquid ammonia was roughly measured by transferring 10 c.c. of a saturated solution

* Garner and Abernethy, *Proc. Roy. Soc.*, 1921, *A*, **99**, 213.

to a weighed crucible and weighing the residue after evaporation of the solvent. It was approximately 0·8 g. in 100 c.c. The solution is at first blue, but changes in the course of a few minutes to a deep purple. A saturated solution is deep red.

Electrolysis of the Solution.—The electrolysis apparatus consisted of a U-tube, provided with two side tubes for the introduction of ammonia and with platinum wire electrodes at the top of each limb. An additional platinum electrode was sealed into one of the limbs at a point a little above the bend in the U-tube. The U-tube was placed in a cryostat of liquid ammonia which could be maintained at a temperature 1° or 2° lower than that of ammonia boiling under atmospheric pressure. After the introduction of a solution of *m*-dinitrobenzene into the U-tube, the two upper electrodes were connected to a 220-volt circuit. The solution did not boil when the current was passed through it. With commercial ammonia as a solvent, a stream of bubbles appeared at the cathode, and after about ½ hour the liquid around the cathode was quite colourless and was separated from the rest of the solution by a sharp boundary, which moved downwards as the electrolysis proceeded until it reached the bottom of the cathode limb, at which point it remained, however long the electrolysis continued. Simultaneously, a deepening of the colour in the anode limb occurred and a small amount of solid deposit formed on the anode. Solutions of varying concentration, from nearly saturated to very dilute solutions, were thus examined, and in all cases, on complete electrolysis, there was a sharp boundary separating a coloured anode solution from a colourless cathode solution.

Examination of Cathode Solution.—On evaporation, the cathode solution gave no residue, and therefore the kation on discharge does not give rise to a non-volatile product. Since, however, a conducting volatile substance might have been present in the cathode solution, a series of experiments was conducted in which the resistances of the anode and cathode limbs were measured during the electrolysis. The electrolysis was interrupted for a few minutes while these measurements were being made: t = time of electrolysis in hours; R_c and R_a = resistance of cathode and anode solutions, respectively, in ohms; concentration = *ca.* 0·0053 g. of dinitrobenzene in 11 c.c.

t.	R_c.	R_a.	t.	R_c.	R_a.
0	49,030	44,510	61	719,600	31,770
4	63,130	38,320	89	1,371,000	—
30	308,100	35,690	∞	4,770,000	—
51	657,500	34,770			

The resistance of the cathode limb at the end of the electrolysis

was so high as to render it improbable that it contained any substance other than anhydrous ammonia.

With anhydrous ammonia as a solvent, on beginning the electrolysis it was just possible to see tiny bubbles of gas rising from the cathode, but these ceased to form after a minute or two. The amount of gas was certainly much less than would have been anticipated had the nitro-compound combined with the solvent to give rise to an ammonium salt of a pseudo-acid.

If a solution of ammonium chloride in ammonia of half the molecular concentration of the solution of *m*-dinitrobenzene be electrolysed, a copious stream of hydrogen appears at the cathode, incomparably larger than that from the solution of the nitro-compound.

It can, however, be urged that the hydrogen is used up in reduction of the nitro-compound, but if this were so no gas would be liberated when a small amount of water is present, as in the experiments with commercial ammonia, for this also should be used up in reduction. With regard to this possibility, it should also be mentioned that more than one-third of the nitro-compound is transported from the cathode solution by the current during an experiment. The amount of current thus employed should simultaneously transfer ammonium ions to the cathode and produce sufficient hydrogen to reduce a very large proportion of *m*-dinitrobenzene, the reduction product of which should be present in the residue after evaporation. Since the solute after the electrolysis melted at 88—89° and consisted almost entirely of unchanged *m*-dinitrobenzene, reduction, if it occurred at all, could not have occurred to the extent mentioned above. Hence the kation in a solution of *m*-dinitrobenzene cannot be NH_4.

Conductivities of the Dinitro-benzenes and -toluenes in Liquid Ammonia.

The methods employed in the preparation of anhydrous ammonia and its condensation in the conductivity cell need no special description here, since they were almost identical with those devised by Kraus and Franklin (*Amer. Chem. J.*, 1900, 23, 277). On a few points of detail their methods were slightly modified. The tap connecting the upper condenser for liquid ammonia with the conductivity cell was completely enclosed by a chamber through which air, dried by passage through liquid air, could be passed continuously. This prevented the intrusion of water through this tap during the mixing of the solute and liquid ammonia. The air regulator of Kraus was replaced by a toluene regulator, which was found to function much better. The temperature of the

cryostat was regulated by controlling the rate of streaming of air through a fine capillary jet. The conductivities were measured by means of an alternating current supplied by a Whetham double rotating commutator and a decade bridge.

Conductivity Measurements with m-*Dinitrobenzene.*—In some of the earlier work considerable difficulties arose due to the slow rate at which the conductivities attained constant values. The measurement of conductivities at a series of dilutions from $V = 60$ to $V = 160{,}000$ litres per g.-mol. required 20 hours of continuous readings. Also, although the results agreed with those of Kraus up to dilutions of 4,000, at the highest dilutions our results were much higher owing to the entrance of water from the tap above-mentioned and of volatile substances from the phosphoric oxide (even when this had been purified with ozone) used in drying the air by which the liquid was stirred. The best results obtained with this arrangement were as follows, V being the dilution in litres and μ the molecular conductivity:

V	74·67	131·0	230·0	404·0	709·6	1247	2189
μ	86·52	98·24	116·0	134·5	154·7	172·7	189·3
V	3844	6751	11,860	20,830	36,580	64,240	112,800
μ	206·0	236·0	250·9	267·9	279·4	297·0	325·5

These difficulties were overcome after the tap had been modified and the air dried by passage through a coil immersed in liquid air, but the time taken to reach equilibrium was so long in the case of the dinitrotoluenes that it became evident that the method of attack based on determinations of conductivities at each dilution would be extremely laborious. Since measurements of the rate of change of conductivity were likely to produce results of equal value and with less expenditure of effort, this method of investigation was adopted.

Rate of Change of Conductivities with Time.—The nitro-benzenes and -toluenes were kindly supplied to us by Dr. O. L. Brady, either in the pure state or of such a degree of purity that only a few further crystallisations were needed.

Experiments were made on the velocity of ionisation at the dilutions $V = 208{\cdot}1$ and $416{\cdot}2$ litres per g.-mol. for each of the nine substances. The requisite quantity of the finely-ground solid was introduced into the bulb of the apparatus. In washing down the solid into the conductivity cell, a portion of the fine light powder was occasionally blown to the top of the bulb, where it was inclined to adhere. This led to a slight source of error in some of the measurements (1 to 2%). As it was only desired to make a preliminary survey of the field, modifications were not made in the apparatus to remove this source of error. The solution was stirred by bubbling

nitrogen through it until no trace of solid could be seen in the cell, and complete solution was ensured by stirring between each of the first half-dozen readings. The cell was then enclosed until the end of the experiment. Readings were thereafter taken over several hours. The moment of introducing the first drop of ammonia into the conductivity vessel was in each case taken as the initial time.

The melting point of the residue after evaporation of the solution after a determination, except in the case of 2 : 4-dinitrotoluene, was never more than about 2° below the melting point of the pure substance. Even the small amount of change which does occur is probably to be accounted for by the action of moisture during the evaporation of the liquid ammonia in the open air. The agreement for duplicate experiments was good, except for 2 : 4-dinitrotoluene, where the velocity of change was subject to fluctuations due to an unknown cause.

In the summary of the results given below, the *m*-compounds are treated separately, only a few of the experimental readings being given. The others are shown on the curves. The velocity coefficient $k = 1/t \,.\, \log_e\{(\mu_0 - \mu_M)/(\mu_t - \mu_M)\}$, where μ_M is the conductivity after equilibrium has been reached. For the highly dissociated nitro-derivatives, the equation gives fairly concordant values for k, but it breaks down for 2 : 6-dinitrotoluene, which is ionised only to the extent of 1—2%. (The conductivity at infinite dilution is about 236 mhos.) It is somewhat surprising that the equation for a reaction of the first order fits so well, especially as the velocity of the back reaction, that of the combination of the ions to give undissociated ammoniate (see equation, p. 1228), has been ignored. The methods adopted in the treatment of simultaneous reactions could be applied here, were the values of x and the numbers of charges on the ions known. Relations based on assumption of simple values for these numbers do not, however, fit the experimental curves.

TABLE II.

m-*Derivatives*.

2 : 6-*Dinitrotoluene*.							
V=208·1.	t mins.	11	24	54	108	162	∞
	μ	1·18	1·84	2·68	3·60	4·15	4·5
	k	0·028	0·021	0·017	0·015	0·016	
V=416·2.	t mins.	14	20	52	107	171	∞
	μ	1·51	1·90	3·10	4·07	4·53	4·9
	k	0·029	0·025	0·019	0·015	0·015	
3 : 5-*Dinitrotoluene*.							
V=208·1.	t mins.	12	15	20	25	32	∞
	μ	41·3	48·2	54·4	57·2	59·4	62·0
	k	0·092	0·100	0·105	0·103	0·99	
V=416·2.	t mins.	21	24	29	44		∞
	μ	79·2	81·7	84·4	88·2		91·5
	k	0·096	0·093	0·088	0·075		

2 : 4-*Dinitrotoluene.*

$V=208{\cdot}1$.	t mins.	16	27	33	52	95	153	223	∞	
	μ	24·6	36·9	43·4	50·5	89·0	110·1	122·1	133·0	
	k	0·0128	0·0120	0·0120	0·0119	0·0116	0·0115	0·0126		
$V=416{\cdot}2$.	t mins.	14	31	46	74	97	159	190	249	∞
	μ	21·1	42·2	56·8	80·2	93·7	121	130	141	152
	k	0·0107	0·0105	0·0102	0·0101	0·0099	0·0100	0·0102	0·0105	

m-*Dinitrobenzene.*

$V=208{\cdot}1$.	t mins.	10	12	16	22	∞	
	μ	84·3	89·4	98·3	106	112	
	k	0·140	0·133	0·131	0·133		
$V=416{\cdot}2$.	t mins.	10	13	17	22	24	∞
	μ	96·8	109	118	123	126	132
	k	0·132	0·134	0·132	0·134	0·129	

A summary of the conductivity changes for those substances undergoing ionisation at a constant rate is given in Table III. Of these substances, 3 : 5- and 2 : 5-dinitrotoluene undergo the second type of ionisation at the greatest rate. The constant rate of change is due neither to oxygen nor to catalysis by the walls or platinum electrodes, for the velocities are not influenced when the solution is stirred.

TABLE III.

o- *and* p-*Derivatives* (*including* 3 : 5-*dinitrotoluene also*).

Nitro-compound.	Initial conductivity max. $V=208{\cdot}1$.	Initial conductivity max. $V=416{\cdot}2$.	Rate of change per hour (mean).
3 : 5-Dinitrotoluene	133	152	3·7
2 : 5- ,,	3·5	6·5	8·5
2 : 3- ,,	0·45	0·7	0·45
3 : 4- ,,	0·5	0·7	0·85
o-Dinitrobenzene	0·5	1·2	1·0
p- ,,	0·3	0·75	0·8

Summary.

The mechanism of the ionisation of the isomeric dinitro-toluenes and -benzenes in liquid ammonia has been investigated. These nitro-derivatives undergo two distinct types of ionisation, which proceed at measurable velocities. One occurs according to the equation $R(NO_2)_2+xNH_3 \rightleftharpoons R(NO_2)_2,xNH_3 \rightleftharpoons R(NO_2^{--})_2+xNH_3^+$, and the other possibly with the production of a pseudo-acid. The former is characteristic of compounds with two nitro-groups in the *m*-position to one another, and proceeds with a velocity which follows the relation for a reaction of the first order. The addition compound formed from the *m*-derivatives is blue or purple.

The second type of ionisation process is typical of compounds with the nitro-groups in the *o*- and *p*-positions to each other, and proceeds at a rate which is independent of the concentration. 3 : 5-Dinitrotoluene is anomalous in that it shows both types of

change, and the *o*- and *p*-derivatives give slight initial conductivities which may be interpreted as due to the first reaction.

The maximum conductivities at any dilution are a measure of the degree of ionisation of the nitro-groups, and hence of their electronegative character. The nitro-groups of the *m*- are much more negative than those of the *o*- and *p*-derivatives. The methyl group in the *m*-position lowers, and in the *o*- and *p*-positions raises, the negative character of the nitro-group. 2 : 6-Dinitrotoluene forms an exception to these rules.

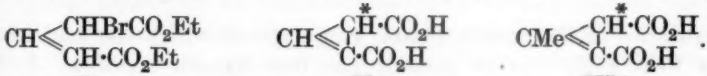
One of us (C. C. S.) wishes to acknowledge the assistance he has received from the Department of Scientific and Industrial Research in carrying out this work.

THE WILLIAM RAMSAY INORGANIC AND PHYSICAL CHEMISTRY LABORATORIES,
UNIVERSITY COLLEGE, LONDON. [*Received, April 3rd*, 1925.]

CLXVIII.—*The Conditions underlying the Formation of Unsaturated and Cyclic Compounds from Halogenated Open-chain Derivatives. Part VII. The Influence of the Phenyl Group on the Formation of the* cyclo*Propene Ring.*

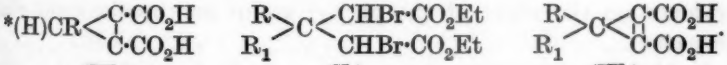
By WILHELM HAERDI and JOCELYN FIELD THORPE.

IT is a remarkable fact that the formation of the *cyclo*propene ring (type II) can be effected with the greatest ease when a mobile hydrogen atom remains in the system produced, that is to say, whenever the ring formed is of the semi-aromatic or glutaconic type, and that when this is not the case it does not appear possible to build up this unsaturated structure. Thus Farmer and Ingold (J., 1923, **123**, 330) found no difficulty in obtaining the acid (II) from α-bromoglutaconic ester (I) and Feist (*Ber.*, 1893, **26**, 750)



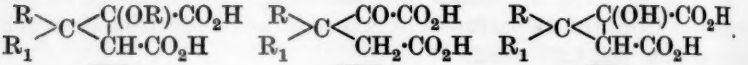
(I.) (II.) (III.)

prepared the acid (III) quite easily from bromo*iso*dehydracetic ester. It will be noticed that both of the acids (II) and (III) contain the mobile hydrogen atom, marked *, which enables them to pass into the semi-aromatic form (IV).



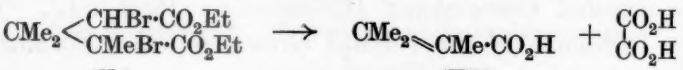
(IV.) (V.) (VI.)

If, however, the conditions are such as to prohibit the existence of this mobile hydrogen within the system, all efforts made to introduce the unsaturated bond into the *cyclo*propane ring fail and in every case the reaction pursues another course. For example (reaction 1), when the dibromo-esters of type (V) lose hydrogen bromide (2 mols.) they do not pass into the acid (VI) or a derivative of it, but yield, in accordance with the value of the group RR_1 and its effect on the carbon tetrahedral angle, either the alkyloxy-derivative (VII), the keto-acid (VIII), or the hydroxy-ring acid (IX).



(VII.) (VIII.) (IX.)

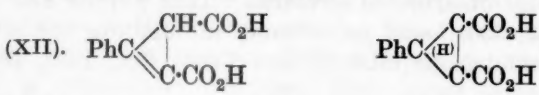
On the other hand (reaction 2), when there exists no tendency to form substances of the above type and when the production of the semi-aromatic system is prohibited, the dibromo-esters undergo fission and yield definite products of degradation. Thus the dibromo-ester (X) yields trimethylacrylic acid (XI) and oxalic acid when treated with potassium hydroxide (Pandya and Thorpe,



(X.) (XI.)

J., 1923, **123**, 2852) and a similar decomposition has recently been recorded in the case of the ββ-dimethyl-α-ethyl derivative (Kon, Smith, and Thorpe, this vol., p. 567).

The object of the experiments described in the present paper was to prepare an acid of formula (XII) which, in its semi-aromatic form, would have the structure (XIII)—in the hope that it would supply further evidence in support of our views regarding the

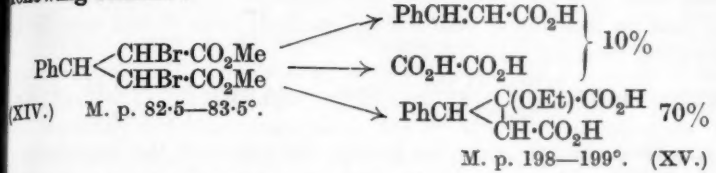


(XII.) (XIII.)

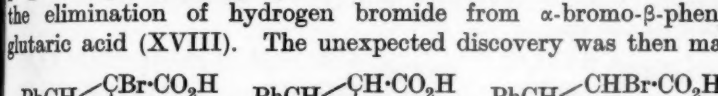
structure of the semi-aromatic ring type of which the acid known as Feist's (III) is at present the best known member. It was expected that the phenyl group in the β-position would confer increased stability on the normal (semi-aromatic) form of the acid as it does in the case of β-phenylglutaconic acid (J., 1912, **101**, 856). Although we were unsuccessful in our attempts to prepare this acid, we, nevertheless, obtained some remarkable evidence on the effect of the phenyl group on three-carbon ring formation.

In the first instance, attempts were made to prepare the acid

(XII or XIII) by the elimination of two molecules of hydrogen bromide from the dibromo-ester (XIV), but the substance underwent both reactions (1) and (2) when treated with alcoholic potassium hydroxide and yielded a result in accordance with the following scheme :

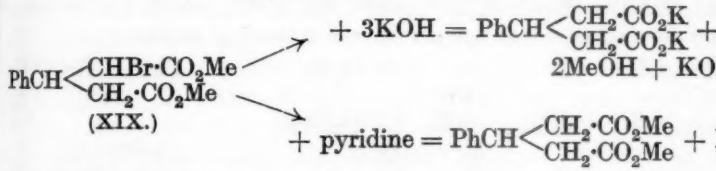


It was then decided to attack the problem by eliminating one molecule of hydrogen bromide from β-bromo-3-phenyl*cyclo*propane-1 : 2-dicarboxylic acid (XVI) and an attempt was made to prepare 3-phenyl*cyclo*propane-1 : 2-dicarboxylic acid (XVII) by the elimination of hydrogen bromide from α-bromo-β-phenylglutaric acid (XVIII). The unexpected discovery was then made



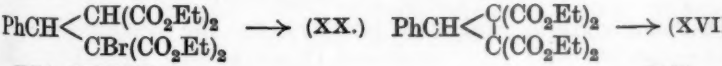
that this bromoglutaric acid (XVIII) contains an active bromine atom and that, in consequence, it is quantitatively converted into β-phenylglutaric acid by potassium hydroxide.

It is very remarkable that the bromine in this compound should also be removed by hot pyridine and that the equations are practic-

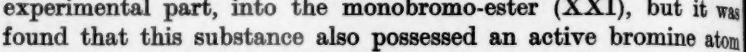


ally quantitative. It has not yet been ascertained what change the pyridine undergoes in this reaction. It is worthy of note that no trace of β-phenylglutaconic acid could be isolated in this way.

Other methods of preparing phenyl*cyclo*propanedicarboxylic acid (XVII) were then investigated and it was ultimately obtained in good quantity by the methods of Buchner (from diazoacetic ester and ethyl cinnamate) and, more readily, by the hydrolysis of ethyl phenyl*cyclo*propanetetracarboxylate (XX) prepared by Kötz and Stahlmann (*J. pr. Chem.*, 1908, 75, 488), in accordance with the scheme :

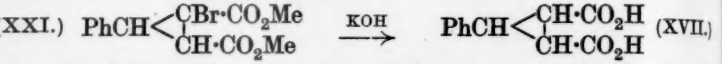


Theoretically the acid (XVII) should exist in three stereochemical modifications, but only one, the *cis-trans* form, has been isolated. This acid can be converted by a special method, described in the experimental part, into the monobromo-ester (XXI), but it was found that this substance also possessed an active bromine atom and that on treatment with potassium hydroxide it was completely converted into the acid (XVII).



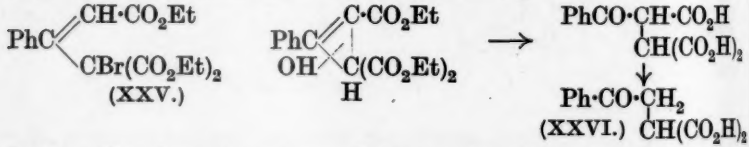
(XXI.) $PhCH<\begin{matrix}CBr\cdot CO_2Me\\ CH\cdot CO_2Me\end{matrix}$ $\xrightarrow{KOH}$ $PhCH<\begin{matrix}CH\cdot CO_2H\\ CH\cdot CO_2H\end{matrix}$ (XVII.)

It was then thought that the bromo-derivative of the tricarboxylic acid (XXII) might eliminate hydrogen bromide in the required direction, but it was found that the acid which has been described under this name in the literature and was prepared by Buchner by the hydrolysis of the ester (XXIII) is in reality carboxyphenylparaconic acid (XXIV), the hydrolysis of the ester having led to fission of the ring:



$PhCH<\begin{matrix}CH\cdot CO_2Et\\ C(CO_2Et)_2\end{matrix}$ (XXIII.) $PhCH<\begin{matrix}CH\cdot CO_2H\\ C(CO_2H)_2\end{matrix}$ (XXII.) $PhCH(O\cdot CO\cdot CH\cdot CO_2H)\cdot CH\cdot CO_2H$ (XXIV.)

Finally, an attempt was made to prepare the required acid by the hydrolysis of the product formed by the elimination of hydrogen bromide from the ester (XXV). No difficulty was experienced in preparing this bromo-derivative, but it was found to undergo deep-seated decomposition when treated with aqueous potassium hydroxide, the chief product being benzoyl*iso*succinic acid (XXVI) (Bischoff, *Ber.*, 1883, **16**, 1045), which had evidently been formed in accordance with the following scheme:



$PhC(CH\cdot CO_2Et)(CBr(CO_2Et)_2)$ (XXV.) $PhC(C\cdot CO_2Et)(OH)(C(CO_2Et)_2)H$ $\rightarrow$ $PhCO\cdot CH(CO_2H)\cdot CH(CO_2H)_2$ $\rightarrow$ $Ph\cdot CO\cdot CH_2\cdot CH(CO_2H)_2$ (XXVI.)

Owing, therefore, to a remarkable series of abnormal reactions the acid (XII) has not yet been obtained, but it is hoped that other experiments which are now in hand will be more successful. The present results are, however, of interest, because they show that the phenyl group, owing doubtless to its marked polar influence, produces effects which are difficult to predict in the present state of our knowledge of these matters.

EXPERIMENTAL.

A. *Derivatives of* β-*Phenylglutaric Acid.*

β-Phenylglutaric acid was prepared by the condensation of benzaldehyde with ethyl malonate (Knoevenagel, *Ber.*, 1898, 31,

2591) and the subsequent addition of ethyl sodiomalonate in ethereal solution (Michael, *J. pr. Chem.*, 1887, **35**, 349). The tetracarboxylic ester produced was then hydrolysed by boiling with hydrochloric acid for 20 hours; it was not found necessary to use hydrobromic acid as recommended by Michael (*loc. cit.*).

Methyl α-Bromo-β-phenylglutarate.—β-Phenylglutaric acid (20·8 g.) was treated with phosphorus pentachloride (42 g.), and bromine (18 g.) slowly added to the product, the reaction being completed by warming on the steam-bath for 2 hours. The mixture was poured into methyl alcohol and the ester isolated in the usual manner. On keeping the ester for several days, a small quantity of methyl αα′-dibromo-β-phenylglutarate, m. p. 82·5—83·5° (see below) was deposited. The main portion of the ester did not solidify and was distilled under reduced pressure. The portion boiling at 175—183°/16 mm. gave on redistillation methyl β-phenylglutarate, b. p. 180—182°/16 mm., m. p. 86—87°. From the higher-boiling oil a fraction, b. p. 204—206°/17 mm., was isolated; it solidified and on crystallisation from light petroleum or a small quantity of methyl alcohol formed tufts of needles, m. p. 83—83·5°, consisting of *methyl α-bromo-β-phenylglutarate* (Found: Br, 24·45. $C_{13}H_{15}O_4Br$ requires Br, 25·4%). Attempts to isolate the monobromo-acid were unsuccessful, because it was always accompanied by the dibromo-compound and the parent acid which prevented it from crystallising. Purification of the acid chloride before bromination (b. p. 171—173°/13 mm.; m. p. 39—40°) is of no advantage.

Methyl αα′-Dibromo-β-phenylglutarate (XIV).—The bromination of β-phenylglutaric acid was carried out in the manner described above, a double quantity of bromine being used; the reaction was complete in about 6 hours. Scarcely any acid ester was formed; the neutral oil solidified on cooling in a freezing mixture, but melted below room temperature. It was purified by distillation under reduced pressure, b. p. 215—220°/20 mm., and solidified in the receiver; on crystallisation from light petroleum or methyl alcohol, short, stout prisms, m. p. 82·5—83·5°, were obtained (Found: Br, 40·4. $C_{13}H_{14}O_4Br_2$ requires Br, 40·6%).

Ethyl αα′-Dibromo-β-phenylglutarate was prepared by pouring the dibromination product into ethyl alcohol and was obtained as a viscid liquid which did not solidify (Found: Br, 37·1. $C_{15}H_{18}O_4Br_2$ requires Br, 37·9%).

Lactone of Ethyl α-Bromo-α′-hydroxy-β-phenylglutarate.—This substance was produced when the dibromo-ethyl ester was distilled under reduced pressure, ethyl bromide being eliminated; it boiled at 230—234°/21 mm. and did not solidify (Found: Br. 25·85. $C_{13}H_{13}O_4Br$ requires Br, 25·6%).

αα'-Dibromo-β-phenylglutaric acid was obtained by pouring the dibromination product into warm water containing a little hydrobromic acid, the solution being decolorised with animal charcoal and evaporated. On standing for several weeks, short prisms, m. p. 192—193°, were deposited, readily soluble in alcohol and ether, less so in hydrobromic acid (Found: Br, 43·9. $C_{11}H_{10}O_4Br_2$ requires Br, 43·7%).

Hydrolysis of the Bromo-compounds.—1. Fifteen grams of the monobromo-ester dissolved in a little methyl alcohol were added to a boiling solution of 30 g. of potassium hydroxide in 16 c.c. of water, the boiling being continued for 10 minutes. The cooled solution was diluted, the neutral impurities were removed by means of ether, and an excess of dilute sulphuric acid was added, the solution being then extracted with ether. The extract on evaporation gave a brown syrup from which a few crystals separated on keeping; these on crystallisation from benzene formed plates, m. p. 138—139°, and consisted of β-phenylglutaric acid. The remainder of the syrup was esterified with ethyl alcohol, the greater part of the ester boiling at 186—188°/13 mm. and yielding pure β-phenylglutaric acid on hydrolysis with barium hydroxide (Found: C, 63·6; H, 5·8. Calc., C, 63·5; H, 5·8%); the acid was identified by direct comparison with a genuine specimen.

2. The monobromo-ester (6 g.) was boiled for 2 hours with pure pyridine (40 g.), and the mixture was cooled and poured into ice-cold dilute hydrochloric acid; extraction with ether gave an oil which boiled almost completely between 175—185°/16 mm. (3·5 g.), 179—182° on redistillation, and solidified in the receiver; it crystallised from light petroleum in stout prisms, m. p. 86—87°, and consisted of methyl β-phenylglutarate (Found: C, 66·4; H, 6·8. Calc., C, 66·1; H, 6·9%). The fraction boiling above 185° (0·5 g.), which solidified, was the unchanged monobromo-ester.

3. The dibromo-ester (35 g.) was treated with alcoholic potassium hydroxide as described above. On acidifying the reaction product, a small quantity of a very dark oil separated which was removed by filtration; from the clear solution ether extracted 16 g. of a syrup which partially solidified. The solid was freed from oil by means of porous porcelain and fractionally crystallised from ether, benzene, and xylene, when two fractions were obtained. The lower-melting fraction consisted of oxalic acid, which was identified in the usual way (Found: in hydrated form, C, 19·2; H, 4·8. Calc., C, 19·05; H, 4·8%). The higher-melting substance, on crystallisation from ether and light petroleum, formed prisms, m. p. 198—199°, consisting of *2-ethoxy-3-phenylcyclopropane-1 : 2-dicarboxylic acid* (XV) [Found: C, 62·3; H, 5·65;

titration, 13·17 c.c. of *N*/20-NaOH. Ag in silver salt, 47·8. $C_{13}H_{14}O_5$ (dibasic) requires C, 62·4; H, 5·6%; 12·99 c.c. $C_{13}H_{12}O_5Ag_2$ requires Ag, 48·3%). The acid is readily soluble in water, alcohol, or ether, sparingly soluble in benzene or xylene, and insoluble in chloroform or light petroleum; it is stable towards cold alkaline permanganate for more than 24 hours. The *methyl* ester boils at 175—179°/13 mm. (Found: C, 64·85; H, 6·2. $C_{15}H_{18}O_5$ requires C, 64·75; H, 6·5%), and the *ethyl* ester at 184—190°/14 mm. (Found: C, 66·4; H, 6·7. $C_{17}H_{22}O_5$ requires C, 66·6; H, 7·2%). The original acid is obtained by hydrolysing these esters either with potassium hydroxide or with hydrochloric acid.

The porous plates used in the isolation of the ethoxy-acid and oxalic acid were extracted with ether, the recovered syrup was esterified, and the esters were fractionated under reduced pressure. A portion boiled at 110—115°/17 mm., the main fraction at 170—182°/17 mm., and only traces above this temperature. The lowest fraction gave on hydrolysis with 12% sodium hydroxide an acid, forming needles, m. p. 53—54°, consisting of Liebermann's cinnamic acid (Michael, *Ber.*, 1901, **34**, 3655), a mixture of *allo-* and *iso*-cinnamic acids [Found: C, 72·6; H, 5·8; titration, 14·96 c.c. of *N*/20-NaOH. Calc. (monobasic), C, 73·0; H, 5·4%; 14·87 c.c.), which can be separated into two forms, m. p. 63—64° and 54—55°, respectively; the mixture, on treatment with bromine in chloroform, yields αβ-dibromocinnamic acid, m. p. 196—197° (Found: Br, 51·9. Calc., Br, 51·6%). The ester, b. p. 170—182°/17 mm., was hydrolysed and gave the ethoxy-ring acid, m. p. 198—199°.

4. The bromolactonic ester gave the same hydrolysis products as the dibromo-ester, but the yield of cinnamic and oxalic acids increased at the expense of that of the cyclic acid.

B. *Derivatives of* 3-*Phenyl*cyclo*propane*-1 : 2-*dicarboxylic Acid.*

3-Phenyl*cyclo*propane-1 : 2-dicarboxylic acid was prepared by Kötz and Stahlmann's method (*loc. cit.*), which was found to be preferable to that of Buchner (*Ber.*, 1888, 21, 2646); the acid prepared by either method melted at 175—176° and on distillation under reduced pressure gave the anhydride, m. p. 134°.

Monobromination.—Methyl 1-*Bromo*-3-*phenyl*cyclo*propane*-1 : 2-*dicarboxylate.* The acid (5·5 g.) was converted into the acid chloride by means of phosphorus pentachloride, and 4·8 g. of bromine were slowly added, traces of iodine and iron filings being introduced as catalysts; the temperature was maintained at 120—130° until one-quarter of the bromine had been added, after which the reaction

proceeded spontaneously; scarcely any hydrogen bromide was evolved. On pouring the reaction mixture into ice-cold methyl alcohol, 4·5 g. of a brown powder separated which was collected; on adding water, an oil was precipitated consisting of a neutral (3 g.) and an acid fraction (1 g.). The brown powder was purified by dissolving in benzene and fractionally precipitating with petroleum; all the fractions obtained were, however, amorphous, coloured, and did not possess a definite m. p. The analysis suggested that addition of bromine with fission of the ring had taken place [Found: Br, 38·9 (in light brown sample), 39·25 (in dark brown sample). $C_{13}H_{14}O_4Br_2$ requires Br, 40·6%]. The neutral, oily bromo-derivative did not solidify; it contained 36·26% of bromine.

The cyclic acid was brominated in the absence of a catalyst, but in the light of a powerful arc-lamp, the temperature being kept at 125° for ½ hour, then at 140° for ½ hour, and the product was worked up as usual. The acid fraction consisted of the *monobromo-acid* ester, m. p. 175—176° [Found: Br, 26·5; titration, 7·92 c.c. of *N*/20-NaOH. $C_{12}H_{11}O_4Br$ (monobasic) requires Br, 26·7%; 7·45 c.c.) The neutral ester (5·5 g.) was an oil which solidified in a freezing mixture, but melted again at room temperature; it could not be distilled without decomposition (Found: Br, 26·4. $C_{13}H_{13}O_4Br$ requires Br, 25·6%).

The monobromination was also carried out in the absence of a catalyst and without the aid of an arc-lamp, but the products were resinous; the reaction took 4 hours at 100°.

Dibromination.—The acid was dibrominated, an arc-lamp being used to accelerate the reaction; this was complete in 6 hours, the temperature being kept at 130—140°. The reaction product, which was partly resinous, was poured into water and freed from tarry matter by means of animal charcoal. The concentrated solution slowly deposited a small quantity of solid, which was purified by washing with ether, dissolving in alkali and reprecipitating. On crystallisation from much ether, small cubes, m. p. 227—228° (0·3 g.) were obtained (Found: Br, 27·3; titration, 16·5 c.c. of *N*/20-NaOH). These results point to a monobromo-acid or a bromolactonic acid [$C_{11}H_9O_4Br$ (dibasic) requires Br, 28·1%; 17·00 c.c. of *N*/20-NaOH].

Hydrolysis of the Bromo-compounds.—The monobromo-ester was hydrolysed exactly as described on p. 1242. On extracting the acidified product with ether and evaporating the extract an oil was obtained which deposited some crystals on standing; these after purification melted at 175—176° and consisted of phenyl-*cyclo*propanedicarboxylic acid. The syrupy portion of the product was esterified with ethyl alcohol and the ester fractionated,

the main portion boiling at 192—205°/16 mm.; this was hydrolysed by means of 12% sodium hydroxide, and the acid so obtained rubbed with a little alcohol. It solidified completely and consisted of the acid, m. p. 175—176°.

The same acid was obtained on hydrolysing the monobromo-ester by means of hot alcoholic potassium hydroxide.

C. *Derivatives of* β-*Phenylglutaconic Acid.*

Phenylpropiolic acid was prepared by Perkin's method (J., 1884, **45**, 172), converted into the ester, b. p. 150—153°/16 mm., by means of alcohol and sulphuric acid, and condensed with ethyl sodiomalonate (Michael, *J. pr. Chem.*, 1895, **49**, 22). The ethyl α-carbethoxy-β-phenylglutaconate so produced could be distilled without decomposition; it yielded β-phenylglutaconic acid, m. p. 154—155°, on hydrolysis with barium hydroxide.

Ethyl α-Carbethoxy-α'-bromo-β-phenylglutaconate.—The tricarboxylic ester was brominated under the conditions used by Kötz (*loc. cit.*) in the preparation of β-phenyl*cyclo*propanedicarboxylic acid; 43 g. of bromo-ester were obtained from 33·4 g. of initial material; the crude ester usually contains a slight excess of bromine (Found: Br, 20·0, 22·85, 21·4. $C_{18}H_{21}O_6Br$ requires Br, 19·4%).

Hydrolysis of the Bromo-ester.—The ester (15 g.) was added to a boiling solution of potassium hydroxide (16 g. in 24 c.c. of water), and the mixture boiled for 20 minutes. The cooled mixture was freed from neutral impurities by extraction with ether and gave on acidification a 60—70% yield of benzoyl*iso*succinic acid (XXVI), m. p. 177—178° (Found: C, 59·6; H, 4·75; Ag in silver salt, 50·0; titration, 6·85 c.c. of *N*/20-NaOH. Calc., C, 59·6; H, 4·5; Ag, 49·5%; 6·78 c.c.). The acid on boiling with hydrochloric acid passes into β-benzoylpropionic acid, m. p. 117°. The *ester*, prepared with the aid of sulphuric acid, boils at 185—195°/20 mm. (decomp.), a red coloration being developed; it yields the original acid on hydrolysis with barium hydroxide.

2. The bromo-ester (44 g.) dissolved in a little alcohol was added to a boiling solution of potassium hydroxide (50 g.) in alcohol (100 g.), the mixture boiled under reflux for 35 minutes, then freed from alcohol by evaporation. The residue was dissolved in water, acidified, and extracted with ether, the extract on evaporation yielding a viscous, brown syrup. This was esterified with the aid of sulphuric acid and the mixed esters were fractionated, a small fraction being obtained at 100—168°/16 mm. and a larger one at 170—190°/16 mm.; decomposition and an intense red coloration of the residue were observed towards the end of the distillation. The main fraction gave on redistillation 6 g. of ethyl

β-benzoylpropionate, b. p. 171—173° (Found: C, 69·2; H, 6·5. Calc., C, 68·9; H, 6·8%). Hydrolysis of the ester with dilute sodium hydroxide gave the corresponding acid, m. p. 116—117° (Found: C, 67·3; H, 5·8; Ag in silver salt, 37·8. Calc., C, 67·4; H, 5·6; Ag, 37·9%). The oxime had m. p. 133·5—134·5° (Found: C, 62·3; H, 5·8; N, 7·4. Calc., C, 62·2; H, 5·7; N, 7·25%).

3. A similar result was obtained by treating the bromo-ester with methyl-alcoholic potassium hydroxide; the yield of benzoyl-*iso*succinic acid was somewhat lower.

4. The bromo-ester was kept with the theoretical quantity of alcoholic ammonia for 6 hours, but no reaction occurred; on standing for 2 days, a substance containing both nitrogen and bromine separated.

Condensation of Ethyl Dibromohydrocinnamate and Ethyl Sodiomalonate.

The condensation was carried out as described by Buchner and Dessauer (*Ber.*, 1892, 25, 1153) for the methyl esters. The mixture of esters obtained was fractionated under 17 mm. pressure, when the following fractions were obtained: (1) 130—165°, 6 g.; (2) up to 198°, 8 g.; (3) up to 205°, 6 g.; (4) up to 215°, 45 g.; (5) above 215°, 3 g. Fraction (1) consisted of ethyl cinnamate, identified in the form of ethyl dibromohydrocinnamate, m. p. 74—75°, and traces of ethyl malonate. Fractions (2) and (3) partially solidified; the solid had m. p. 76° after crystallisation and was identified as ethyl ethanetetracarboxylate; the liquid portion of fraction (2) yielded phenylpropiolic acid, m. p. 136°, on hydrolysis with sodium hydroxide, whilst the liquid portion of fraction (3) gave acetophenone on hydrolysis with hydrochloric acid; this was probably derived by the decomposition of ethyl benzoylacetate or ethyl ethoxycinnamate.

The main fraction boiled at 208—211°/16 mm. on refractionation and consisted of *ethyl phenylcyclopropanetricarboxylate* (XXIII) (Found: C, 64·3; H, 6·75. $C_{12}H_{22}O_6$ requires C, 64·7; H, 6·95%).

The ester was hydrolysed with alcoholic potassium hydroxide; the carboxyphenylparaconic acid (XXIV) obtained gradually solidified and was crystallised from ethyl acetate and benzene or petroleum; it formed prisms, m. p. 88°, which contained four molecules of water of crystallisation. On keeping in a vacuum, the anhydrous form, m. p. 187—188° (decomp.), was obtained; it can be purified by dissolving in ethyl acetate and gradually evaporating the solvent (Found: C, 57·6; H, 4·3. $C_{12}H_{10}O_6$ requires C, 57·6; H, 4·0%). On boiling with hydrochloric acid, the acid, m. p. 187—188°, passes into phenylparaconic acid, m. p. 99—100°; this

acid is also obtained by the direct hydrolysis of the cyclic ester with hydrochloric acid. The elimination of the carboxyl group from the acid, m. p. 187—188°, is, however, best achieved by heating it with twelve times its weight of naphthalene at 185—190° until the evolution of carbon dioxide ceases, the yield of phenylparaconic acid being quantitative. Both acids yield phenyl*iso*crotonic acid on distillation.

The acid, m. p. 187—188° (4 g.), was converted into the acid chloride by means of phosphorus pentachloride, bromine added (2·6 g.), and the brominated acid chloride poured into warm water; after removal of resinous impurities, the solution was evaporated to a small bulk, when colourless prisms, m. p. 99°, of bromophenylparaconic acid separated (Fittig, *Annalen*, 1889, **256**, 76) (Found: Br, 28·3. Calc., Br, 28·1%).

Condensation of Ethyl Dibromocinnamate with Ethyl Sodiomalonate.

(1) With two molecules of sodium ethoxide. The reaction mixture was heated for 25 hours on the steam-bath. The neutral portion of the reaction product was distilled under 17 mm. pressure, and the main fractions were obtained at 110—160° and 160—190°. The lower of these consisted of ethyl ethanetetracarboxylate, m. p. 76°, whilst the liquid consisted of the unchanged bromo-ester. Scarcely any ring compound appeared to be formed.

(2) With one molecule of sodium ethoxide. The reaction was carried out under the same conditions. A high fraction, b. p. 217—219°/18 mm. after redistillation, was isolated. It was free from halogen and reduced permanganate, although it did not react with bromine in chloroform solution (Found: C, 63·6; H, 6·55. $C_{20}H_{26}O_7$ requires C, 63·5; H, 6·9%). On hydrolysis with alcoholic potassium hydroxide the ester yielded an *acid*, m. p. 171—172°, probably containing a lactone ring [Found: C, 60·3; H, 5·0; Ag (in the silver salt), 45·2. $C_{14}H_{12}O_6$ requires C, 60·4; H, 5·0%. $C_{14}H_{10}O_6Ag_2$ requires Ag, 43·9%]. On boiling with hydrochloric acid, the substance passes into phenylparaconic acid; its structure has not yet been determined.

(3) In the absence of alcohol a mixture of ethyl malonate (16 g.) and "molecular" sodium (2·3 g.) in dry ether was kept for 8 hours, ethyl dibromocinnamate (33·5 g.) was then added, and the mixture kept for 2 hours. The esters were isolated and distilled in the usual manner. The main fraction boiled on redistillation at 201—205°/16 mm. and consisted of the ester (XXV) (Found: Br, 18·9. $C_{18}H_{21}O_6Br$ requires Br, 19·4%), whilst the next higher fraction contained less bromine, due to an admixture of ethyl ethanetetra-

carboxylate, which soon separated in crystals. The ester reduced permanganate, but did not react with bromine in chloroform solution. Several attempts were made to effect ring-closure by the action of finely divided sodium in benzene or toluene, but the ester was recovered unchanged with the exception of a part which resinified. The bromo-ester was then subjected to hydrolysis with 60% potassium hydroxide; the only product isolated was carboxyphenylparaconic acid, m. p. 187—188° after drying in a vacuum [Found: C, 57·4; N, 4·0; Ag (in the silver salt), 54·7. Calc., C, 57·6; H, 4·0%. $C_{12}H_9O_7Ag_3$ requires Ag, 55·0%), which yielded phenylparaconic acid on boiling with hydrochloric acid.

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CLXIX.—*The Directing Influence of the Methanesulphonyl Group.*

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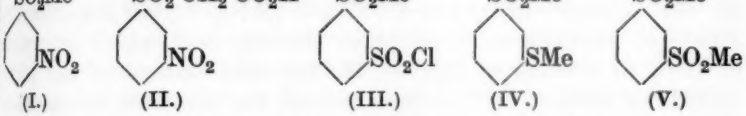
ACCORDING to Martinet and Haehl (*Compt. rend.*, 1921, **173**, 775) the nitration of diphenylsulphone yields the 3 : 3′-dinitro-derivative. This behaviour accords with that of benzenesulphonic acid, which on substitution yields mainly the meta-compounds. It is noteworthy, therefore, that a para-directive influence has been assigned to the methanesulphonyl group of phenylmethylsulphone, which, according to Bourgeois and Abraham (*Rec. trav. chim.*, 1911, **30**, 407), yields 4-bromophenylmethylsulphone when treated with bromine in presence of ferric chloride. Further investigation of the matter was needed, for the result of Bourgeois and Abraham indicates the possibility of obtaining the *o*-disulphonyl group by direct substitution, the process being one which is only seldom realised. Moreover, this apparent difference in character between the sulphonyl or the benzenesulphonyl group and the methanesulphonyl group, if firmly established, would be of considerable interest in its theoretical aspect. Experiments on the nitration, sulphonation, and bromination of this methylsulphone which have now been made have led only to meta-derivatives, and confirmation of the para-directive influence of the methanesulphonyl group is entirely lacking.

Nitration of phenylmethylsulphone gave a *mononitro*-derivative, m. p. about 141° (crude), 146° (purified), which was identical with the 3-nitrophenylmethylsulphone (I), m. p. 146°, obtained from the methylation of 3-nitrobenzenesulphinic acid and different from

the 4-nitrophenylmethylsulphone, m. p. 141°, which Zincke (*Annalen*, 1913, **400**, 16) obtained by methylation of 4-nitrobenzenesulphinic acid.

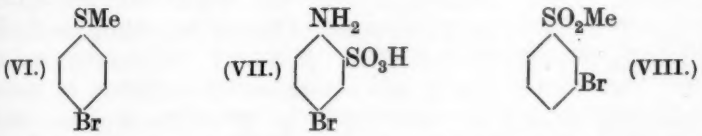
The orientation of the nitration product of phenylsulphoneacetic acid (II) was similar; it was proved by conversion into the methylsulphone.



(I.) (II.) (III.) (IV.) (V.)

Sulphonation of phenylmethylsulphone also gave the meta-derivative (III), the constitution of which was established by conversion through the methyl sulphide (IV) into the dimethylsulphone (V), the latter being identical with the meta-derivative obtained from benzene-*m*-disulphonyl chloride by conversion into the sulphinic acid and subsequent methylation.

Bromination of phenylmethylsulphone by Bourgeois and Abraham's method (*loc. cit.*) led to a substance, m. p. 103°, which was not, as those authors state, 4-bromophenylmethylsulphone, m. p. 103°, but was identical with 3-bromophenylmethylsulphone (VIII), m. p. 103°, which we prepared from 4-bromoaniline-2-sulphonic acid (VII) by eliminating the amino-group and converting the sulphonic acid into the methylsulphone by usual methods. Bourgeois and Abraham prepared 4-bromophenylmethylsulphone by oxidising the corresponding sulphide (VI); we obtained it from 4-bromobenzenesulphinic acid.



(VI.) (VII.) (VIII.)

From the comparative state of purity of the crude products of nitration and sulphonation, it seems that appreciable quantities of ortho- or para-compounds are not formed under the conditions adopted.

Experimental.

3-*Nitrophenylmethylsulphone* (I). — (*a*) From phenylmethylsulphone. Powdered potassium nitrate (1·5 mols.) was slowly added to a stirred solution of phenylmethylsulphone (1 mol.) in six times its weight of cold sulphuric acid. The mixture was kept at 90° for 1 hour, the solid product being then isolated by the addition of water. A further small quantity was removed from

the liquid with ether (yield 96—98%, m. p. 141° approx.). The substance crystallised from hot water in colourless needles, m. p. 146°.

(*b*) From 3-nitrobenzenesulphinic acid. Limpricht (*Ber.*, 1892, **25**, 75, 3477) prepared this acid by reducing 3-nitrobenzenesulphonyl chloride with sodium sulphite. A purer product is more readily obtained by reduction with a sodium mercaptide according to the scheme $RSO_2Cl + 2R'SNa = (R'S)_2 + RSO_2Na + NaCl$. Powdered 3-nitrobenzenesulphonyl chloride was added in small portions to a warm solution of the requisite amount of the mercaptide in alcohol. When the reaction was complete the sodium chloride was collected and the liquid was evaporated, water being continually added until all alcohol had been expelled. The insoluble disulphide was removed and the sparingly soluble silver sulphinate was obtained from the aqueous liquor. After purification, the silver salt was treated with methyl iodide in the usual manner. The product, 3-*nitrophenylmethylsulphone*, melted after purification at 146°, whether heated alone or mixed with the product obtained by nitration of the sulphone (Found: N, 7·3; S, 15·8. $C_7H_7O_4NS$ requires N, 7·0; S, 15·9%).

For comparison, the 2-nitro- and 4-nitro-derivatives were prepared by methylation of the corresponding sulphinic acids. The melting points (106° and 141°) recorded for these substances in the literature (Claasz, *Ber.*, 1912, **45**, 1023; Zincke, *Annalen*, 1913, **400**, 16) were confirmed.

3-*Nitrophenylsulphoneacetic Acid* (II).—The nitration of phenylsulphoneacetic acid was conducted as in the case of phenylmethylsulphone. After purification from hot water the product had m. p. 62° approx., the exact point of fusion depending on the rate of heating (Found: N, 5·8. Calc., N, 5·7%). Limpricht (*Annalen*, 1897, **294**, 243) prepared this substance by oxidation of the corresponding alcohol and recorded m. p. 57°. The acid was heated at 150°, the liberation of carbon dioxide being rapid; the residue, m. p. 146°, was 3-nitrophenylmethylsulphone.

m-*Phenylenedimethylsulphone* (V).—(*a*) From benzene-*m*-disulphonyl chloride. Conversion of this substance into the ammonium disulphinate was effected by Suzuki's method (*J. Coll. Sci. Tokyo*, 1908, **25**, xiv, 1). When the silver salt of this sulphinic acid was treated with methyl iodide in boiling methyl alcohol, the required disulphone was obtained. After purification from hot acetic acid it formed colourless prisms, m. p. 196°. Zincke prepared (*Ber.*, 1912, **45**, 3471) this substance by oxidising the dimethylthiol and recorded the same melting point.

(*b*) From phenylmethylsulphone. A solution of phenylmethyl-

sulphone in four times its weight of chlorosulphonic acid was kept at 110—120° for 1 hour. The cooled mixture was poured over ice, and the precipitated oil, which solidified (m. p. 90—91°), crystallised from cold acetone and water, m-*chlorosulphonylphenylmethylsulphone* (III) separating in colourless plates, m. p. 94° (Found: Cl, 14·0; S, 25·4. $C_7H_7O_4ClS_2$ requires Cl, 13·9; S, 25·2%). This sulphonyl chloride was reduced to the mercaptan in the usual manner with excess of tin and hydrochloric acid, the aqueous liquor was removed, and the solid mass of tin and mercaptan extracted with alcohol. From this solution the mercaptan (m. p. 69°) was isolated and converted to the methylthiol (IV) as described below.

This mercaptan was also prepared in the following manner. A solution of the sulphinic acid was obtained by treating the sulphonyl chloride with concentrated aqueous sodium sulphite. The acid was not isolated, but by treatment in this solution at 90° with a little hydrogen iodide in presence of an excess of mineral acid it was converted into the disulphoxide. *Phenylmethylsulphone* m-*disulphoxide*, $(CH_3{\cdot}SO_2{\cdot}C_6H_4)_2S_2O_2$, was thus obtained in colourless needles, m. p. 200° (Found: C, 41·0; H, 3·4. $C_{14}H_{14}O_6S_4$ requires C, 41·3; H, 3·5%). This disulphoxide was rapidly attacked by boiling aqueous alkali hydroxide, yielding a solution of the alkali sulphinate, whilst the disulphide separated. *Phenylmethylsulphone* m-*disulphide*, $(CH_3{\cdot}SO_2{\cdot}C_6H_4)S_2$, separated from acetone–water in pale yellow needles, m. p. 120° (Found: C, 44·7; H, 3·7. $C_{14}H_{14}O_4S_5$ requires C, 44·9; H, 3·8%). Hydrolysis of this disulphide by further treatment with boiling aqueous alkali readily furnished a solution of the mercaptide (compare J., 1921, **119**, 1794), from which the mercaptan was obtained in the usual manner.

The mercaptan, prepared by either of these methods, was treated with methyl sulphate in methyl alcohol containing the requisite amount of sodium methoxide. Thus m-*methylthiolphenylmethylsulphone* (IV) was obtained; it separated from light petroleum in colourless plates, m. p. 53° (Found: C, 47·3; H, 4·9. $C_8H_{10}O_2S_2$ requires C, 47·5; H, 5·0%).

Oxidation of the thioether was effected by hydrogen peroxide in warm glacial acetic acid; after purification, the product melted at 196° whether heated alone or with a sample of the material prepared from benzene-*m*-disulphonyl chloride (Found: C, 41·1; H, 4·2. $C_8H_{10}O_4S_2$ requires C, 41·0; H, 4·3%).

3-*Bromophenylmethylsulphone* (VIII).—(*a*) By bromination of phenylmethylsulphone. The conditions used were similar to those employed by Bourgeois and Abraham (*loc. cit.*) except that a somewhat higher temperature (130°) was found necessary.

(*b*) From 3-bromobenzenesulphonic acid. The diazonium salt

obtained from 20 g. of 4-bromoaniline-2-sulphonic acid was decomposed by warming the alcoholic solution in presence of a small quantity of potassium carbonate. When the reacting mixture had cooled, sodium 3-bromobenzenesulphonate separated; a further quantity was isolated from the solution (yield, 16 g. of crude material). The purified sodium salt was converted into the acid chloride, and the latter was shaken with a concentrated solution of sodium sulphite. When the chloride had dissolved, the solution was mixed with an excess of sulphuric acid, the liberated sulphinic acid being then removed with ether. This acid (m. p. 73°), on treatment with methyl sulphate in presence of alkali, yielded 3-bromophenylmethylsulphone. A sample of the purified product melted at 103°, whether heated alone or mixed with the product yielded by the bromination of phenylmethylsulphone (Found: C, 35·5; H, 3·1. $C_7H_7O_2BrS$ requires C, 35·7; H, 3·0%).

4-*Bromophenylmethylsulphone* was prepared by the interaction of sodium 4-bromobenzenesulphinate with methyl sulphate. After purification, it melted at 103°, but a mixture with an approximately equal amount of the material obtained by brominating phenylmethylsulphone melted indistinctly at about 70° (Found: C, 35·4; H, 3·0. $C_7H_7O_2BrS$ requires C, 35·7; H, 3·0%). The 4-bromobenzenesulphinic acid (m. p. 115°) was prepared from 4-bromobenzenesulphonic acid (Nölting, *Ber.*, 1875, **8**, 594; Hübner, *Annalen*, 1870, **156**, 326) by usual methods. The substance has been previously described by Knoevenagel and Kenner (*Ber.*, 1908, **41**, 3323), who obtained it (m. p. 114°) by sulphinating bromobenzene.

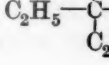
In conclusion, we wish to thank the Department of Scientific and Industrial Research for a grant which has enabled one of us to take part in these experiments.

KING'S COLLEGE, LONDON. [*Received, April 25th*, 1925.]

CLXX.—3 : 3-*Diethylpentane* (*Tetraethylmethane*).

By GILBERT T. MORGAN, SYDNEY RAYMOND CARTER, and ALBERT E. DUCK.

3 : 3-DIETHYLPENTANE or tetraethylmethane is of special interest as having the most symmetrical chemical structure (I) of all the theoretically possible nonanes.



(I.)

From the general and inorganic point of view the hydrocarbon acquires additional significance owing to the circumstance that it may also be regarded as carbon tetraethyl, being the initial member required to complete the following series :

$$C(C_2H_5)_4,\ Si(C_2H_5)_4,\ Ge(C_2H_5)_4,\ Sn(C_2H_5)_4,\ Pb(C_2H_5)_4.$$

This tertiary paraffin has now been synthesised from diethyl ketone by successive applications of the Grignard and Frankland reactions as summarised in the following scheme :

$$(C_2H_5)_2CO \longrightarrow (C_2H_5)_3C{\cdot}OH \longrightarrow (C_2H_5)_3CI \longrightarrow C(C_2H_5)_4.$$

Preparation of 3 : 3-*Diethylpentane.*—Triethylcarbinol, prepared by the Grignard reaction (magnesium ethyl iodide) from diethyl ketone (yield 50%), was saturated with dry hydrogen iodide produced by adding concentrated hydriodic acid to phosphorus triiodide (Möslinger, *Annalen*, 1877, **185**, 55; Jourdan, *ibid.*, 1880, **200**, 104), the liquid being cooled to avoid the formation of unsaturated compounds which are formed on raising the temperature. The brown oil was dried and distilled repeatedly under reduced pressure, when *triethylcarbinyl iodide* was obtained as a colourless liquid which rapidly became brown on exposure (Found : I, 55·3. $C_7H_{15}I$ requires I, 56·15%). The yield of purified triethylcarbinyl iodide was 86% : b. p. 71·2°/16 mm.; corrected b. p. (Siwoloboff's method) 153°/737 mm.; $d_4^{20°}$ 1·42.

Zinc ethiodide was prepared by warming ethyl iodide with an equal weight of dry zinc–copper couple made from Kahlbaum's No. 1 zinc and 1·5% aqueous copper sulphate. On heating the ethiodide in a current of carbon dioxide, zinc diethyl distilled and was collected in a reaction flask to which triethylcarbinyl iodide was slowly added at 0°. After several days, the yellowish-white paste was treated successively with cold water and hydrochloric acid. The supernatant oil (48% by weight) from many operations, when tested with bromine water and alkaline permanganate, always showed the presence of unsaturated compounds. Fuming sulphuric acid (60% SO_3), mixtures of nitric and sulphuric acids, and concentrated sulphuric acid were each employed in the removal of unsaturated by-products, and as the best result was obtained with the last of these reagents, the main batch (146 g.) of crude hydrocarbon was shaken with 60% by weight of cold concentrated sulphuric acid and after washing and drying over caustic potash was distilled under reduced pressure. After five fractionations, a product was obtained boiling at 45—47·5°/19 mm. (Found : C, 83·8, 83·7; H, 15·3, 15·5. C_9H_{20} requires C, 84·3; H, 15·7%).

The foregoing processes were found to give the best yields of 3 : 3-diethylpentane, but before this optimum result was attained

the following alternative methods had been tried without success: (1) magnesium ethyl iodide gave no reaction in the cold with triethylcarbinyl iodide, and warming led to the formation of unsaturated products derived from the decomposition of the tertiary iodide; (2) diethyldichloromethane, prepared from diethyl ketone and phosphorus pentachloride, when treated with excess of zinc diethyl at 70°, gave a very poor yield of saturated hydrocarbon; (3) zinc diethyl was poured into triethylcarbinyl iodide; the reaction was extremely vigorous and the product was very unsaturated.

Chemical properties. 3 : 3-Diethylpentane did not decolorise bromine water or alkaline permanganate either in the cold or on boiling for ½ hour and was not attacked by warm concentrated sulphuric or nitric acid. In its chemical inertness it showed the characteristic behaviour of a paraffin.

Physical properties. The hydrocarbon is a clear, colourless liquid having a faint camphoraceous odour, a property which is frequently observed in compounds containing a tertiary carbon atom (Durrans, *Perf. and Essent. Oil Rec.*, 1919, **10**, 104). It was completely soluble in alcohol and ether, but not so soluble in alcohol alone.

Melting point. When cooled with a mixture of ether and solid carbon dioxide, 3 : 3-diethylpentane solidified to a crystalline solid, which was allowed to melt partly, the liquid being drained away. This operation was repeated six times until the residue had a constant melting point, determined by plotting temperature (registered by a pentane thermometer) against time, both while freezing and melting. The curves showed a distinct change of slope at $-40°$ to $-42°$, so that the m. p. is $-41° \pm 1°$.

The portion having the highest melting point was used in determining the physical properties described below. A specimen which had not been purified by freezing gave slightly different values; for instance, the densities showed a difference of one unit in the third decimal place.

Boiling point (by Siwoloboff's method), correcting for exposed stem, was 138·1°/740 mm. With further corrections to 760 mm. at 0°, b. p. = 139·2°/760 mm.

Density, determined by the pyknometer and compared with water at 4° :

15°.	20°.	25°.	30°.	40°.
0·75651	0·75222	0·74868	0·74478	0·73758

Hence the coefficient of cubic expansion between 15° and 30° = 0·001044.

The molecular volume, V_m, at 15° was 128·16/0·75651 = 169·4

c.c. The values of the atomic volumes of the constituent elements as given by Traube are C = 9·9 c.c., H = 3·1 c.c. and hence the calculated V_m for 3 : 3-diethylpentane is 151·1 c.c. or the co-volume is 169·4 — 151·1 = 18·3. For monomeric complexity, the normal value of the co-volume is 25·9 c.c., which suggests that the hydrocarbon is associated, the association factor being (25·9—18·3)/12·95 = 1·58. But since other physical properties do not indicate association, it is probable that the constitutional effects of symmetrical configuration of the hydrocarbon affect the molecular volume, and for comparison this quantity has been calculated for the other known nonanes, the value of the density being reduced in each case to 15°/4°. The arbitrary coefficient, 0·001031 per 1° for unit density, has been assumed for this purpose.

	d (corr. $\frac{15°}{4°}$).	V_m.	Co-volume.
n-Nonane [4]	0·7213	177·7	26·6
3-Methyloctane [5]	0·7214	177·7	26·6
4-Methyloctane [3]	0·7314	175·2	24·1
2 : 4-Dimethylheptane [2]	0·7200	178·0	26·9
2 : 5-Dimethylheptane [1]	0·7184	178·4	27·3
2 : 6-Dimethylheptane [1]	0·7116	180·1	29·0
2 : 2 : 5-Trimethylhexane [7]	0·7118	180·1	29·0
4-Ethylheptane [6]	0·7445	172·1	21·0
3 : 3-*Diethylpentane*	0·7565	169·4	18·3

[1] Clarke, *J. Amer. Chem. Soc.*, 1912, **34**, 54. [2] *Idem*, *ibid.*, **34**, 60. [3] *Idem*, *ibid.*, **34**, 680. [4] *Idem*, *ibid.*, 1915, **37**, 2536. [5] Hardin, *J. Chim. Phys.*, 1906, **6**, 179. [6] Oberreit, *Ber.*, 1896, **29**, 2003. [7] Kishner, *Abs. Journ. Chem. Soc.*, 1913, **104**, 1164.

2 : 6-Dimethylheptane and 2 : 2 : 5-trimethylhexane with terminal *iso*- and tertiary groupings are the least compact. 4-Ethylheptane, on the other hand, with a more symmetrical arrangement of three branching chains, has a much lower molecular volume, whereas in the new isomeride, 3 : 3-diethylpentane with the most symmetrical constitution, V_m is the least of all.

According to Le Bas, "the relative volumes of the atoms remain the same in members of a homologous series although their actual volumes differ from one another." Hence $V_m = nS$, where n is the number of hydrogen equivalents. Thus for 3 : 3-diethylpentane $V_m = 169·41 = 56S$ or $S = 3·0251$, and consequently carbon = 12·10 (since C = 4H). Assuming that the quaternary grouping of $(C_2H_5)_4$ round the central atom has the same value, $V_a(C_2H_5)_4$, in tetraethyl derivatives of other elements of the fourth periodic series, one can calculate the atomic volume of the central atom from $V_m - V_a(C_2H_5)_4$. This assumption may not be strictly valid because the central carbon atom may have a volume different from that of the carbon in the four ethyl groups, but the value for carbon can only be computed from the total number of carbon atoms in

the molecule. However, on this assumption the atomic volumes will have a relative value.

	$d_{4^\circ}^{15^\circ}$ (corr.).	V_m.	Atomic volume of central atom.
$C(C_2H_5)_4$	0·7565	169·4	12·1
$Si(C_2H_5)_4$	0·7903 [1]	182·8	25·5
$Ge(C_2H_5)_4$	0·9980 [6]	189·1	31·8
$Sn(C_2H_5)_4$	1·1898 [2]	197·4	40·1
	(1·4089) [3]	(166·7)	(9·4)
$Pb(C_2H_5)_4$	1·6619 [4]	194·5	37·2
	1·62 [5]	199·5	42·2

[1] Mean of Abati and Ladenburg's values. [2] Ghira. [3] Gladstone; this value does not fall into line. [4] Ghira. [5] Burton. [6] Dennis and Hance. References given in table on p. 1259.

When these atomic volumes are plotted against atomic weights, a curve is obtained similar to that given by Le Bas (" Molecular Volumes of Liquid Chemical Compounds," p. 236). This author, who discusses only the data at the melting and boiling points, gives the formula $d_0/d_t = 1 + 0{\cdot}46$ (1 — 273/b. p.) for calculating the molecular volume at the boiling point (P., 1914, **30**, 86).

The density of 3 : 3-diethylpentane at 0° was calculated from its coefficient of expansion and from the above formula at the boiling point, $d = 0{\cdot}6683$ and $V_m = 191{\cdot}76$, whilst the calculated volume from the data given by Le Bas for carbon and hydrogen is 206·3. Thus the experimental value indicates a contraction of 14·54.

Vapour density measurements carried out with the Victor Meyer apparatus, using an air jacket regulated to 220°, gave vapour densities of 61·9, 62·0, and 64·4, respectively; mean = 62·8. C_9H_{20} requires 64·1, hence the hydrocarbon is not associated in the vapour state.

Surface tension. The rise of 3 : 3-diethylpentane in a capillary tube was measured over a range of temperatures, the radius of the tube being determined by comparative experiments with pure benzene. The resulting values of the surface tension (γ) and the molecular surface energy ($\gamma V_m^{2/3}$) are given in the following table :

t.	20°	25°	30°	40°
γ	22·92	22·45	21·99	21·23
$\gamma V_m^{2/3}$	704·5	692·2	680·4	661·1

The two series of values (γ and $\gamma V_m^{2/3}$) plotted against temperature both give practically straight-line graphs.

In non-associated liquids, the molecular surface energy is a linear function of temperature, the temperature coefficient, k, being a constant of the order of 2·12. The experimental data for this coefficient gave a mean value of $k = 2{\cdot}17$ between 20° and 40°, leading to the conclusion that 3 : 3-diethylpentane is not associated in the liquid state.

The following hydrocarbons have been investigated previously by the capillary tube method and the results are added for comparison.

Hexane : $\gamma = 18{\cdot}54$ (8·2°), $\gamma = 13{\cdot}34$ (62·5°), $k = 2{\cdot}11$.

n-Octane : $\gamma = 21{\cdot}31$ (15·5°), $\gamma = 18{\cdot}56$ (46·3°), $k = 2{\cdot}217$.

Compressibility of 3 : 3-*diethylpentane.* The compactness of the molecule as deduced from the present evidence is probably connected with the large attraction between the carbon atoms (Richards, *J. Amer. Chem. Soc.*, 1914, **36**, 2438).

Moreover, it appears to be a general rule that the less volatile and more dense of two isomerides has the smaller compressibility, consequently the fact that 3 : 3-diethylpentane has a comparatively high boiling point and the greatest density of the nonanes would indicate that its compressibility would be small.

Refractivity. By means of a Pulfrich refractometer, the refractive index, n, for sodium light at 18° was found to be 1·42057; whence $R_L = 43{\cdot}06$ and $r_G = 71{\cdot}48$ (calc., 43·53 and 71·79, respectively).

The refractive indices for the other nonanes (Clarke, *J. Amer. Chem. Soc.*, 1912, **34**, 56; Kishner, *loc. cit.*) are as follows :

	n_D at 25°.		n_D at 25°.
n-Nonane	1·4125	2 : 5-Dimethylheptane	1·4020
4-Methyloctane	1·4027	2 : 2 : 5-Trimethylhexane .	1·3987
2 : 4-Dimethylheptane	1·4014	4-Ethylheptane (at 20°) ...	1·41564

3 : 3-Diethylpentane, the densest isomeride, has the highest refractive index.

Relationship between Physical Properties and Chemical Structure of 3 : 3-*Diethylpentane and Allied Paraffins.*

The eleven known hydrocarbons containing the quaternary linking, that is, having four radicals attached to one carbon atom, are set out on page 1258. The properties of each compound are compared with those of the normal chain isomerides and the differences in boiling point and density are given under Δ b. p. and Δ d respectively.

The tendency to closer packing is evidenced by the increased density except where the repulsive effect of *iso*-groups at the ends of the chain neutralises this effect, as in II, III, V, and IX. The influence of branch chain configuration on physical properties of hydrocarbons has been studied by L. Clarke (*J. Amer. Chem. Soc.*, 1911, **33**, 523). The more symmetrical grouping, where the chains attached to the central atom are of more equal lengths, increases the density considerably and in such cases the lowering in boiling point is lessened.

		B. p.	Δ b. p.	d (corr. $\frac{15°}{4°}$).	Δ d $\frac{15°}{4°}$.
	C_5H_{12} *n*-Pentane [1]	36·3°			
I.	2 : 2-Dimethylpropane [5] (Tetramethylmethane)	9·5	−26·8°	—	—
	C_6H_{14} *n*-Hexane [2, 3]	68·9		0·6667	
II.	2 : 2-Dimethylbutane [10, 6] (Trimethylethylmethane)	49·6	−19·3	0·6538	−0·0129
	C_7H_{16} *n*-Heptane [4, 9]	98·4		0·6885	
III.	2 : 2-Dimethylpentane [11] (Trimethylpropylmethane)	78 (743)	−20·4	0·6776	−0·0109
IV.	3 : 3-Dimethylpentane [8] (Dimethyldiethylmethane)	86—87	−11·9	0·7000	+0·0115
V.	2 : 2 : 3-Trimethylbutane [7] (Trimethyl-*iso*propylmethane)	80·75	−17·7	0·6945	+0·0060
	C_8H_{18} *n*-Octane [13]	124·7		0·7062	
VI.	3-Methyl-3-ethylpentane [12] (Triethylmethylmethane)	118·7 (750)	−6·0	0·7159	+0·0097
VII.	2 : 2 : 3-Trimethylpentane [14] (Trimethyl-*sec.*-butylmethane)	110·6	−14·1	0·7213	+0·0151
VIII.	2 : 2 : 3 : 3-Tetramethylbutane [16] (Hexamethylmethane)	106	−18·7		
	C_9H_{20} *n*-Nonane [15]	150·5		0·7213	
IX.	2 : 2 : 5-Trimethylhexane [17] (Trimethyl-*iso*amylmethane)	124·5 (763)	−26·0	0·7118	−0·0095
X.	2 : 3 : 3 : 4-Tetramethylpentane (Dimethyldi-*iso*propylmethane)	130	−20·0	—	—
XI.	3 : 3-*Diethylpentane* (Tetraethylmethane)	139·2	−11·3	0·7565	+0·0352

[1] Young, J., 1897, **71**, 446. [2] *Idem*, *ibid.*, 1898, **73**, 906. [3] Francis and Young, J., 1898, **73**, 930. [4] *Idem*, *ibid.*, 1898, **73**, 921. [5] Lwow, *Z.*, 1870, 520. [6] Van Risseghem, *Bull. Soc. chim.*, 1922, **31**, 62. [7] Chavanne and Lejeune, *ibid.*, 1922, **31**, 98. [8] Friedel and Ladenburg, *Annalen*, 1867, **142**, 310. [9] Thorpe, *ibid.*, 1879, **198**, 364. [10] Markovnikov, *Ber.*, 1899, **32**, 1445. [11] *Idem*, *ibid.*, 1900, **33**, 1908. [12] Tafel and Jurgens, *ibid.*, 1909, **42**, 2548. [13] Clarke, *J. Amer. Chem. Soc.*, 1912, **34**, 54. [14] *Idem*, *ibid.*, 1912, **34**, 170. [15] *Idem*, *ibid.*, 1915, **37**, 2536. [16] Henry, *Compt. rend.*, 1906, **142**, 1075. [17] Kishner, *loc. cit.*

The substituted methanes show an increase in boiling point as the methyl groups are successively replaced by the ethyl radical, but the increment diminishes as the replacement progresses:

$C(CH_3)_4$, b. p. 9·5°; $C(CH_3)_3{\cdot}C_2H_5$, b. p. 49·6°; $C(CH_3)_2(C_2H_5)_2$, b. p. 86—87°; $C(CH_3)(C_2H_5)_3$, b. p. 118·7°; $C(C_2H_5)_4$, b. p. 139·2°.

Tetraethylmethane having no *iso*-groups, is very compact and

symmetrical. This is borne out in the high density (it is the most dense of the nonanes) and the comparatively small lowering of the boiling point.

The quaternary grouping when symmetrical has the peculiar effect of restricting the range of liquid existence, as will be seen by a comparison of the melting points and boiling points with those of their normal isomerides.

	M. p.	B. p.
n-Pentane	−130·8°	36·3°
2 : 2-Dimethylpropane	−20	9·5
n-Nonane	−51	150·5
3 : 3-Diethylpentane	−41	139·2
n-Octane	−57·4	124·7
2 : 2 : 3 : 3-Tetramethylbutane (double quaternary grouping)	+103—+104	106

3 : 3-*Diethylpentane* (*Carbon Tetraethyl*) *compared with its Homologues of the Periodic Group.*

The physical properties of the higher members of the following homologous series have only been very incompletely investigated, and the following table shows the changes in melting point, boiling point, density, and refractive index with increase in atomic weight of the central atom.

	M. p.	B. p.	Density.	Ref. index. n_D.
Carbon tetraethyl	−41°	139·2°	0·7565 (15°/4°)	1·42057 (18°)
Silicon ,,	—	153 [4]	0·8341 (0°) [5] 0·7689 (22·7°/4°) [9]	1·42628 (22·7°) [9]
Germanium ,, [7]	−90	163·5	0·9911 (24·5°/24·5°)	1·407 (18°)
Tin ,,	—	181 [3] 175 [6]	1·18484 (19·1°/4°) [6] 1·4089 (t° ?) [1]	1·46835 (19·1°) [8] 1·5143 (t° ?) [1]
Lead ,,	—	>200 [2] (decomp.)	1·64926 (22·4°/4°) [8] 1·62 [2]	1·51417 (19·1°) [8]

[1] Gladstone, J., 1891, **59**, 293. [2] Buckton, *Annalen*, 1859, **109**, 22. [3] Frankland, *ibid.*, 1859, **111**, 46. [4] Friedel and Crafts, *ibid.*, 1863, **127**, 31. [5] Ladenburg, *ibid.*, 1872, **164**, 331. [6] Pfeiffer and Schnurmann, *Ber.*, 1904, **37**, 320. [7] Dennis and Hance, *J. Amer. Chem. Soc.*, 1925, **47**, 370. [8] Ghira, *Gazzetta*, 1894, **24**, i, 309. [9] Abati, *ibid.*, 1897, **27**, ii, 452.

Materials are being accumulated for a further comparative study of the physical properties of 3 : 3-diethylpentane, its homologues, and its organo-metallic analogues.

The authors' thanks are due to Messrs. Brunner Mond and Company, Ltd., and to the Government Grant Committee of the Royal Society for grants which have helped to defray the expense of this investigation.

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[*Received, March 19th*, 1925.]

CLXXI.—*The Rotatory Dispersive Power of Organic Compounds. Part XVI. Halogen Derivatives of Camphor. Optical Superposition in the Camphor Series.*

By JOHN OUTRAM CUTTER, HENRY BURGESS, and THOMAS MARTIN LOWRY.

1. *Scope of the Experiments.*

THE experiments of this series were undertaken with the idea of investigating the influence (i) on the rotatory power of camphor and (ii) on its rotatory dispersion, of the creation of a new asymmetric carbon atom by the introduction of a halogen in the α- or α′-position. Valuable materials for this purpose had been provided by the isolation of a series of α′-derivatives (J., 1915, **107**, 1382; 1922, **121**, 633; 1923, **123**, 1867), with the help of which the influence of the new asymmetric atom could be studied when it is producing a negative instead of a positive effect on the rotatory power. The results of these two lines of investigation are set out in §§ 2 and 3.

2. *Numerical Relations between Rotatory Powers.*

The data summarised in Table I show that

(i) The rotatory power of α- and α′-chlorocamphor can be represented by the formula

$$[\alpha]_{5461} = 65{\cdot}5^\circ \pm 24{\cdot}6^\circ \text{ or } [M]_{5461} = 111{\cdot}8^\circ \pm 41{\cdot}9^\circ,$$

whereas the mean of the rotatory powers of camphor and of αα′-dichlorocamphor is $[\alpha]_{5461} = 62{\cdot}1^\circ$ or $[M]_{5461} = 113{\cdot}5^\circ$.

(ii) In the same way, the rotatory power of α- and α′-bromocamphor can be represented by the formula

$$[\alpha]_{5461} = 51{\cdot}8^\circ \pm 98{\cdot}9^\circ \text{ or } [M]_{5461} = 111{\cdot}5^\circ \pm 212{\cdot}6^\circ,$$

whereas the mean of the rotatory powers of camphor and of αα′-dibromocamphor is $[\alpha]_{5461} = 51{\cdot}3^\circ$ or $[M]_{5461} = 113{\cdot}6^\circ$.

(iii) Again, the rotatory power of αβ- and α′β-dibromocamphor can be represented by the formula

$$[\alpha]_{5461} = 8{\cdot}8^\circ \pm 91{\cdot}9^\circ \text{ or } [M]_{5461} = 25{\cdot}7^\circ \pm 270^\circ,$$

whereas the mean of the rotatory powers of β-bromocamphor and αα′β-tribromocamphor * is *about* $[\alpha]_{5461} = 12^\circ$ or $[M]_{5461} = 27^\circ$.

In these three cases, it is possible to recognise the general validity of the idea which forms the basis of van 't Hoff's principle of optical superposition; namely, that the various asymmetric atoms each contribute an independent partial rotation to the observed total

* The rotatory power of this compound is so small that the mean values would not be affected greatly by the fact that a different solvent, concentration, and temperature were used for measurements of its rotatory power.

rotation of the molecule. Thus in (i), (ii), and (iii) the mean rotations, representing the rotatory power of the camphor nucleus as modified by a halogen atom in the α- or α′-position, have been calculated by two independent methods; the calculated rotations are seen to agree with one another within narrower limits than those imposed by the uncertainty whether specific or molecular rotations should be used in comparing compounds of unequal molecular weight.* A similar statement may be made in reference

TABLE I.

Rotatory Power of Halogen Derivatives of Camphor.

Substance.	Solvent.	Conc. (g./100 g.).	$[\alpha]_{5461}$.	$[M]_{5461}$.	Mean.	Diff.
Camphor	Benzene	14·06	52·34°	79·7°	[α] 62·1°	19·5°
αα′-Dichlorocamphor *	,,	18·77	71·89	147·3	[M] 113·5	67·6
α-Chlorocamphor	,,	11·09	90·10	153·7	[α] 65·5	49·1
α′- ,,	,,	11·70	40·98	69·9	[M] 111·8	83·8
Camphor	Benzene	14·06	52·34	79·7	[α] 51·3	2·1
αα′-Dibromocamphor	,,	17·41	50·19	147·6	[M] 113·6	67·9
α-Bromocamphor	,,	14·55	150·71	324·2	[α] 51·8	197·7
α′- ,,	,,	14·50	−47·02	−101·1	[M] 111·5	425·3
β-Bromocamphor	Benzene	33·37	21·50	46·2	[α] 12	20
αα′β-Tribromocamphor	‖ Acetone †	2·42 §	$[\alpha]_D^{\infty}$ 2	$[M]_D$ 7·5	[M] 27	39
αβ-Dibromocamphor	Benzene	16·90	100·64	295·8	[α] 8·8	183·7
α′β-Dibromocamphor	,,	16·86	−83·11	−244·3	[M] 25·7	540·0
π-Bromocamphor	‡ Chloroform †	6·32 §	$[\alpha]_D^{15°}$ 116	250	—	—
αα′π-Tribromocamphor	Benzene	2·55 §	91·8	357	—	—
απ-Dibromocamphor	,,	15·49	110·83	325·8	[α] 118·7	−15·8
α′π-Dibromocamphor	,,	6·20	126·63	372·2	[M] 349·0	−46·4

* This specimen was prepared by Mr. H. E. F. Notton.

† We were not able to procure specimens of these two compounds in order to measure their rotatory powers in benzene.

‡ Kipping and Pope (J., 1895, **67**, 382); these authors also give $[\alpha]_D$ = +99·88° for 2·35% in chloroform (*loc. cit.*, p. 379).

§ Grams per 100 c.c. ‖ Armstrong and Lowry, J., 1902, **81**, 1467.

* The practical identity of the *molecular rotations* 147·3° and 147·6° of αα′-dichloro- and αα′-dibromo-camphor, and of the mean molecular rotations 111·8° and 111·5° of the stereoisomeric α- and α′-chloro- and bromo-camphors is very striking and shows that *the influence of the two halogens on the molecular rotatory power of the camphor nucleus is the same*; on the other hand, the *specific rotations* of camphor, 52·3°, α- and α′-bromocamphor, (mean) 51·8°, and αα′-dibromocamphor, 50·2°, are almost equal, although their molecular rotations differ widely.

to the plus or minus influence of the >CHBr group in (ii) and (iii). Nothing of the sort can, however, be detected in the π-compounds, where the rotations of the stereoisomerides

$$[\alpha]_{5461} = 118{\cdot}7^\circ \mp 7{\cdot}9^\circ, [M]_{5461} = 349{\cdot}0^\circ \mp 23{\cdot}2^\circ$$

differ only to a very small extent from one another, and are actually in the opposite order, for solutions in benzene, to the normal order which they show in chloroform; in addition, the rotations in chloroform of the α- and α'-derivatives, instead of being displaced in opposite directions, are *both* higher than the corresponding value for π-bromocamphor in the same solvent. It is therefore obvious that in the π-derivatives the asymmetric system of camphor has been disturbed in some fundamental way, the nature of which is not yet clear, but may be explored further with the help of the measurements of rotatory dispersion.*

3. *Form of the Dispersion Curves.*

The data shown in Tables III to X all exhibit a complex rotatory dispersion, but in every case except one they can be expressed by two terms of Drude's general equation.† The constants of this equation were calculated directly from the rotation data without regard to any theories as to their relation to the absorption bands of the compound, which were only determined accurately

* This point will be discussed in Part XVII.

† Of the ten cases of complex rotatory dispersion now recorded, *three* are of the type (with two partial rotations of similar sign) which is said by Hunter (J., 1924, **125**, 1202) to be "impossible to detect"; *five* more, or one-half of the total, are of the type of which he says that "it will be possible only in rare cases to detect the two terms in the equation"; *one* is too complex to be expressed by a two-term equation; and only *one* is of the totally anomalous type which is described as "the only case in which the form of the dispersion curve may be determined with any degree of confidence." The inaccuracy of these unqualified assertions may be illustrated by the fact that when an attempt was made to fit a one-term equation to the visual readings for α-bromocamphor, the deviation in the calculated value for the last photographic reading, instead of being so small as to be impossible to detect (since the two terms of the equation are of similar sign), amounted to more than half a right angle; and even in the visible region there were systematic deviations which could not have been overlooked by any careful worker. Again, the second type of dispersion, so far from being capable of detection "only in rare cases," is actually the commonest type of all in the camphor series, and may produce even more marked deviations from the requirements of the law of simple rotatory dispersion; thus, in the case of camphor itself, the attempt to fit a simple formula to the visible readings gave rise to an error of more than sixteen right angles in the calculated value corresponding to the last photographic reading (obs. 790°, calc. 2257°, diff. 1467°), although the casual errors were only of the order of about 2°.

at a later stage. The values obtained in this way were as follows:

TABLE II.

Rotatory Dispersion of Halogen Derivatives of Camphor.

	k_1.	k_2.	λ_1^2.	λ_2^2.	λ_1. (Å.U.).	λ_a.* (Å.U.).
α-Chlorocamphor	+12·938	+ 7·5189	0·09882	0	3140	3050
α′- ,,	+13·733	− 9·401	0·10881	0	3300	3100
α-Bromocamphor	+13·276	+19·530	0·10855	0·0562	3290	3120
α′- ,,	+10·232	−26·393	0·10630	0·03525	3260	3140
β- ,,	+ 9·7419	− 8·1869	0·09915	0	3150	2930
αα′-Dibromocamphor	+14·666	− 8·1713	0·11296	0	3770	3230
αβ- ,,	+16·134	+ 5·8907	0·09863	0	3140	3080
α′β- ,,	Not expressed by a two-term equation.					
απ- ,,	+25·163	− 5·741	0·10476	0	3240	3130
α′π- ,,	+34·648	−15·659	0·10470	0	3235	3090

* This column shows the wave-length of maximum absorption of light.

In most cases, the four constants of a two-term equation can be varied to an appreciable extent, in harmony with one another, without introducing any large deviations in the form of the curve,* but this is no longer true of the three-constant equations which (following Drude's usage in the case of quartz) were used in seven out of ten of the above cases; and it is only partly true of the two four-constant equations, since these were based on exceptionally full series of experimental data. This point may be illustrated by referring to the calculation of the formula for the rotatory dispersion of α-bromocamphor in benzene. As originally calculated by us, the constants deduced were as at I below; but, whilst a very close agreement was obtained in the red, yellow, and green regions of the spectrum, nearly all the errors in the violet and ultra-violet regions were negative in sign, although they gave no evidence of "breaking away," since the deviations diminished almost to zero in the last ultra-violet readings, after reaching a maximum of some 2° at about 4000 Å.U. This systematic deviation was corrected † by changing the constants as in II.

	k_1.	k_2.	λ_1^2.	λ_2^2.
I. (Old constants)	13·276	19·428	0·10837	0·05765
II. (New constants)	13·276	19·530	0·10855	0·0562

It will be seen that a very obvious systematic deviation was removed by altering k_2 by 0·1 (a correction of about 1/200), λ_1^2 by 0·00018 (a correction of about 1/600), and λ_2^2 by 0·0014 (a correction of about 1/40). Whilst, therefore, the response of the formula to variations in the different constants is very unequal (*e.g.*, the

* See footnote, Part XV, p. 611.

† We are indebted to Mr. G. O. Owen, B.Sc., for undertaking the calculation of a corrected formula.

formula is far more sensitive to changes in λ_1^2 than in λ_2^2), it looks as if on the average the absolute values of the constants were fixed by the experimental data within perhaps 1%, although in general it is necessary to use four or five significant figures in each constant when calculating the rotations.

A study of the constants leads to the following conclusions.

(a) *The low-frequency term*, which represents the contribution of the ketonic group to the optical activity of the molecule, is always positive, just as in the case of camphor. Its magnitude in the first seven compounds ranged from $k_1 = 10$ to $k_1 = 16$. These values are smaller than those recorded for camphor, but if molecular rotations were used some of them would be larger.

(b) *The high-frequency term*, which can be regarded as representing the sum of the partial rotations of the fixed asymmetric centres, is *negative* in camphor. (i) This term remains negative in β-bromocamphor and in αα′-dibromocamphor, where no new centre of asymmetry is introduced, and the dispersion is quasi-anomalous (this vol., footnote, p. 608) as in the case of camphor itself. (ii) In the compounds which contain a halogen in the α-position, the large positive partial rotations of the new asymmetric carbon atom make the high-frequency term *positive*, so that the two partial rotations are of similar sign. The rotatory dispersion is therefore complex but normal, and is no longer even quasi-anomalous.*

* In view of Hunter's recommendation that "a return to the older system of classification of rotatory dispersion as normal and anomalous" (which has never been abandoned by us) "is eminently desirable," it is necessary to state clearly that, if it is desired to secure a single rigid method of classifying rotatory dispersions, this system is even more inadmissible on practical grounds than the classification which it is proposed to abandon. Accurate diagnosis on the lines suggested depends on the behaviour of the dispersion curves in the region of long wave-lengths, and is therefore not less, but more, difficult than in the case of simple and complex dispersions, where the diagnosis depends on the behaviour of the curves in the region of shorter wave-lengths. Thus "with the experimental means at present at our disposal" we have no method of following a dispersion curve into the infra-red region in order to test whether it is really normal or anomalous, whereas we can test a simple dispersion experimentally right up to the limit of complete transparency in the ultra-violet, which is also the limit of validity of the formula, and so secure a complete solution of the practical problem of determining (apart from all speculative considerations) whether the rotations obey the law of simple dispersion or not. In practice, therefore, the newer system of classification can be based upon direct experimental measurements in the ultra-violet, whilst the older system of classification rests insecurely upon a process of extrapolation from the visible into the infra-red region of the spectrum. Thus, on the assumption that the two-term equation is valid, we can assert that the dispersion of *β*-bromocamphor is *complex but normal*, since $k_1 > k_2$ when $\lambda_1^2 > \lambda_2^2$; but the margin is so narrow that the calculated curve only just fails to cross the axis, and any doubt as to the validity of the

(iii) In the two α′-derivatives, on the other hand, the fixed negative rotation of the camphor molecule is reinforced by the negative partial rotation of the new asymmetric carbon atom. In the case of α′-bromocamphor this reinforcement is sufficient to overbalance the strong positive partial rotation of the ketonic group, with the result that the dispersion curve becomes *totally anomalous*. This case is noteworthy in that *an inflection*, *maximum* and *reversal of sign* have all been recorded simultaneously in the same solution and in a range of wave-lengths covering only half an octave; the exact positions of these anomalies can be calculated from formulæ given in an earlier paper of this series (J., 1915, **107**, 1197) as follows:

Inflection 5455 Å.U. *Maximum* 4710 Å.U. *Reversal* 3890 Å.U.

(c) In the case of α′β-dibromocamphor, where the influence of the new negative partial rotation is so overwhelming that the total rotations are negative throughout the whole range of the observations, it was no longer possible to make use of a two-term equation, probably because the new fixed partial rotation has a different frequency from the old, so that a three-term equation would be required to express the dispersion.

(d) The π-compounds are seen to be abnormal in several respects, since (i) the low-frequency term is much larger than in any of the other halogen derivatives of camphor; (ii) the high-frequency term is negative in *both* of the stereoisomeric απ- and α′π-dibromocamphors; (iii) the reversal of asymmetry in the α-carbon atom is compensated, in a manner not hitherto recorded, by a corresponding change in the low-frequency partial rotation, so that the total rotation is scarcely altered by the reversal of the sign of this atom.

4. *Relation between Rotatory Dispersion and Absorption.*

The publication of the optical rotations now recorded has been held back for more than a year in order to conform to suggestions that the measurements of rotatory dispersion would be of greater value if correlated with measurements of absorption. This correlation was entirely outside the scope of our original programme.

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equation would at once make the extrapolation into the infra-red region so uncertain that we could no longer say whether the dispersion should be classed as normal or anomalous. Again, failure to fit a one-term equation in the region of transparency is already sufficient to prove that a dispersion is not simple but complex; and this is still more clearly true when a two-term equation also fails to fit the data, as in the case of α′β-dibromocamphor. The dispersion of this compound is therefore obviously complex; but it cannot be classified with any degree of certainty as normal or anomalous, since the true form of the dispersion equation is still unknown, and it is therefore impossible to say whether the dispersion curve would or would not cut the axis if produced into the region of long wave-lengths.

Moreover, if it had been included, it would probably have led us into serious error, since, if we had started out with the idea that the characteristic wave-length of the rotation constants is identical with the characteristic wave-length of the absorption bands, we should almost inevitably have succumbed to the temptation to adopt the easy method of using the wave-lengths of the absorption bands as constants in the equations of rotatory dispersion, instead of following the more arduous course of deducing these constants from an independent study of the dispersion data. Fortunately, the whole of the dispersion data had been calculated, and the paper had been submitted for publication, before this subtle temptation was presented to us. We can therefore claim without any reservation that the constants of all the dispersion equations given in the present paper are based upon measurements of optical rotations only, and that, as a result of working on this independent basis, we have been led to the discovery of a systematic discrepancy between the values of the characteristic wave-lengths as deduced from the two types of measurement.

A similar discrepancy to that shown in Table II has already been recorded in Part XIII (J., 1924, **125**, 2521), where it was shown that the rotation constant of the one-term dispersion equation of camphorquinone gives a characteristic wave-length about 50 Å.U. greater than that of the uncorrected value for the head of the band, and again in Part XV (this vol., p. 611), where the low-frequency partial rotation in the two-term equation for a solution of camphor in benzene is controlled by a dispersion constant of which the characteristic wave-length is about 70 Å.U. greater than that recorded for the head of the absorption band. This difference was, moreover, increased to about 140 Å.U. when the high-frequency dispersion constant was neglected in working out a three-constant equation to express the data for a solution of camphor in *cyclo*hexane.

In the present instance we abandoned the attempt to record the absorption spectra in *benzene* (which had been selected as the best available solvent for the measurements of rotatory dispersion) and deliberately made use of solutions in cyclo*hexane*, the transparency of which enabled us to make the measurements of absorption in the ordinary way, instead of by the precarious use of thin films of concentrated solutions. This change of solvent * had

* Attention has already been directed (Gifford and Lowry, *Proc. Roy. Soc.*, 1923, *A*, **104**, 434) to the fact that *cyclo*hexane and benzene differ by less than a degree in their freezing points as well as in their boiling points, a fact which suggests the existence of some analogy of internal structure which is not shown by the conventional classification of the two hydrocarbons as saturated and unsaturated respectively.

already been proved to have no effect on the position of the ketonic band in camphor (Lowry and French, J., 1924, 125, 1924), and we had therefore no reason to suppose that it would affect the position of the band in this series of camphor derivatives.

Table II shows that, if we reserve the case of $\alpha\alpha'$-dibromocamphor for special consideration, the average value of the characteristic wave-length, λ_1, of the low-frequency partial rotation is 3220 Å.U., whilst the average wave-length, λ_a, of the head of the ketonic band is 3080 Å.U. There is therefore a difference of about 140 Å.U. between the two series, just as in the case of camphor in *cyclo*hexane. This discrepancy may again be accounted for by noticing that, when a selective absorption is superposed on a strong general absorption, the observed head of the band will be displaced towards a region of shorter wave-lengths. It is also possible that the omission of the high-frequency dispersion constant in the three-constant equations may tend to increase the value recorded for the low-frequency dispersion constant although the influence of this omission has not yet been studied sufficiently to enable us to draw very definite conclusions in regard to it.* Since, however, these disturbing factors, if operating in the manner suggested, would tend to *increase* the value of λ_1 and to *decrease* the value of λ_a, they would unite in producing discrepancies of the sign actually recorded.† There can therefore be little doubt that the average difference of 140 Å.U. is a fair measure of the effects produced in this way.

Although no great importance can be attached to the study of the individual differences between λ_1 and λ_a, the case of $\alpha\alpha'$-dibromocamphor is sufficiently striking to be picked out from all the others, since an average difference of 140 Å.U. is here increased to more than 500 Å.U. It is noteworthy that the general absorption (which can only be detected with difficulty in the case of camphor) is now so strong that the selective absorption produces little more than a mere " step-out " in the absorption curve, the difference between the maximum and minimum values of $\log\epsilon$ being reduced to 0·1 only, as compared with a value $>1·7$ for a solution of camphor in *cyclo*hexane, where the minimum was not reached at the last recorded wave-length. Although, therefore, the observed head of the ketonic band in $\alpha\alpha'$-dibromocamphor is at a longer wave-length than in any of the other derivatives in the list, we are entitled to suppose that the real maximum of selective absorption would be

* The average difference in the case of the two four-constant equations of Table II is very nearly equal to the average difference in the case of the seven three-constant equations.

† The sentence " Since . . . direction " in Part XV (this vol., p. 612) in which it is implied that the two errors would tend to cancel out is incorrect and should be deleted.

Table III.

Rotations of α- and α′-Chlorocamphor in Benzene at 20°.

(*a*) 11·090 G. of α-chlorocamphor in 100 g. of solution.

Density 0·9018. Length of tube 6 dcm.

$[a] = 1{\cdot}666a$. $[M] = 1{\cdot}866[a]$.

$$[a] = \frac{12{\cdot}938}{\lambda^2 - 0{\cdot}09882} + \frac{7{\cdot}5189}{\lambda^2}.$$

(*b*) 11·6970 G. of α′-chlorocamphor in 100 g. of solution.

Density 0·90405. Length of tube 6 dcm.

$[a] = 1{\cdot}576a$. $[M] = 1{\cdot}866[a]$.

$$[a] = \frac{13{\cdot}733}{\lambda^2 - 0{\cdot}10881} - \frac{9{\cdot}401}{\lambda^2}.$$

Wave-length.		Spec. rot. Obs.	Cal.	Diff.	Spec. rot. Obs.	Cal.	Diff.
Li	6707·8	—	—	—	19·3°	19·4°	−0·1°
Cd	6438·5	58·9°	59·1°	−0·2°	22·1	22·2	−0·1
Zn	6362·3	60·9	60·9	±	23·2	23·2	±
Na	5893·0	73·8	73·7	+0·1	30·5	30·5	±
Hg	5790·7	77·3	77·1	+0·2	—	—	—
Cu	5782·2	77·5	77·4	+0·1	31·6	32·8	−1·2
Hg	5780·1	—	—	—	32·9	32·9	±
Hg	5769·6	78·0	77·9	+0·1	—	—	—
Cu	5700·2	80·2	81·7	−1·5	34·5	34·6	−0·1
Hg	5460·7	90·1	90·1	±	41·0	41·0	±
Cu	5218·2	102·6	102·2	+0·4	49·1	49·5	−0·4
Cu	5153·3	106·0	105·9	+0·1	52·1	52·2	−0·1
Cu	5105·5	109·1	108·8	+0·3	54·2	54·4	−0·2
Cd	5085·8	110·0	110·0	±	55·3	55·3	±
Zn	4810·5	130·8	131·2	−0·4	71·5	71·4	+0·1
Cd	4799·9	131·8	131·5	+0·3	72·3	72·1	+0·2
Fe	*4762*	*133·6*	*134·3*	*−0·7*	—	—	—
Fe	*4730*	—	—	—	*78·8*	*77·5*	*+1·3*
Zn	4722·2	139·2	137·9	+1·3	77·8	78·5	−0·7
Fe	*4548*	—	—	—	*94·6*	*94·6*	±
Fe	*4468*	*166·6*	*165·8*	*+0·8*	—	—	—
Fe	*4426*	—	—	—	*110·3*	*109·7*	*+0·6*
Hg	4358·3	183·2	181·5	+1·7	119·1	119·7	−0·6
Fe	*4320*	—	—	—	*126·1*	*126·1*	±
Fe	*4165*	*216·6*	*216·6*	±	—	—	—

displaced still further towards the visible region if a correction were made for the influence of the strong general absorption. Even this displacement, however, would probably be insufficient to account for a discrepancy of over 500 Å.U., and we may therefore suspect that the neglect of the high-frequency dispersion constant also produces an exceptionally large effect in this case, perhaps because this constant is unusually large, corresponding with the unusual immanence of the general absorption.

5. *Materials and Measurements.*

(*a*) α-Chlorocamphor was crystallised five times from benzene and melted at 94°. α′-Chlorocamphor, crystallised twice from alcohol, retained a slight yellow tint; but since its rotatory power was not altered by recrystallisation it was regarded as sufficiently pure for measurements of dispersion; the sample melted at 118°.

TABLE IV.

Rotations of α-Bromocamphor in Benzene at 20°.

14·5480 G. of α-bromocamphor in 100 g. of solution.

Density 0·92770. Length of tube 6 dcm.

$[a] = 1{\cdot}235a$. $[M] = 2{\cdot}311[a]$. $[a] = \frac{13{\cdot}276}{\lambda^2 - 0{\cdot}10855} + \frac{19{\cdot}53}{\lambda^2 - 0{\cdot}0562}$.

(*a*) Visual Readings.

Wave-length.	Spec. rot. Obs.	Cal.	Diff.
Li 6707·8	88·57°	88·40°	+0·17°
Cd 6438·5	97·79	97·79	±
Zn 6362·3	100·78	100·74	+0·04
Na 5893·0	122·70	122·66	+0·04
Hg 5790·7	128·44	128·39	+0·05
Cu 5782·2	128·88	129·88	±
Hg 5769·6	129·67	129·68	−0·01
Cu 5700·2	133·88	114·89	−0·01
Hg 5460·7	150·71	150·62	+0·09
Cu 5218·2	171·45	171·29	+0·16
Cu 5153·2	177·85	177·69	+0·16
Cu 5105·5	182·89	182·59	+0·30
Cd 5085·8	185·92	185·71	+0·21
Zn 4810·5	219·20	219·27	−0·07
Cd 4799·9	221·15	221·08	+0·07
Zn 4722·2	233·08	232·99	+0·09
Hg 4358·3	309·28	309·73	−0·55

(*b*) Photographic Readings.

Wave-length.	Spec. rot. Obs.	Cal.	Diff.
Fe 5200	*172·9°*	*173·0°*	*−0·1°*
Fe 5024	*191·4*	*191·6*	*−0·2*
Fe 4983·3	*196·4*	*196·4*	±
Fe 4920·5	*203·8*	*204·2*	*−0·4*
Fe 4788·7	*222·3*	*222·5*	*−0·2*
Fe 4632·9	*247·0*	*248·1*	*−1·1*
Fe 4408·4	*296·4*	*295·8*	*+0·6*
Fe 4325·8	*319·8*	*381·1*	*+1·7*
Fe 4234	*345·8*	*346·5*	*−0·7*
Fe 4162	*369·2*	*371·7*	*−2·5*
Fe 4102	*395·2*	*395·8*	*−0·6*
Fe 4065	*413·7*	*412·8*	*+0·9*
Fe 4054·9	*418·6*	*417·6*	*+1·0*
Fe 4001·7	*444·6*	*444·7*	*−0·1*
Fe 3956·7	*469·3*	*471·1*	*−1·8*
Fe 3883·3	*518·7*	*519·9*	*−1·2*
Fe 3852·6	*542·1*	*543·9*	*−1·8*
Fe 3823	*563·1*	*569·4*	*−1·3*
Fe 3798·5	*591·5*	*592·4*	*−0·9*
Fe 3774·8	*617·4*	*616·6*	*+0·8*
Fe 3758	*636·0*	*635·1*	*+0·9*
Fe 3753·6	*640·9*	*640·1*	*+0·8*

α-Bromocamphor was crystallised six times from benzene and melted at 76°. β-Bromocamphor was crystallised three times from benzene and melted at 79°; the melting point and rotatory power were unaltered by the last recrystallisation. αα′-Dibromocamphor was crystallised four times from benzene and dried in the dark; this compound is not very stable and readily assumes a yellow colour. Purified specimens of the other five compounds were already available from earlier researches (J., 1922, **121**, 633; 1923, **123**, 1867).

(*b*) The benzene used as solvent for the first six compounds was purified as described in Part XV. For the remaining four compounds it was purified by a modification of the method of Richards and Shipley (*J. Amer. Chem. Soc.*, 1914, **36**, 1825); it was washed free from thiophen with sulphuric acid, then with water, dried over calcium chloride, and frozen four times, the wet setting-point rising during the purification from 5·20° to 5·40°, 5·48°, 5·52° and 5·51°. The last fraction, when dried over sodium, distilled at 80·00—80·03° (uncorr.), and was kept over sodium.

(*c*) The optical rotations are shown, with calculated values, in Tables III to X. The accuracy of the specific rotations is usually less than that of the original readings, since the reduction factor was generally greater than unity, on account of the low concentration of these solutions, *e.g.*, as compared with the high concentrations which are possible in the case of camphor as a result of its extremely high solubility in organic solvents. In some cases the concentration was limited by the low solubility of one of the two isomerides which it was desired to compare under similar conditions. This limitation does not apply in the case of β-bromocamphor (Table V), the concentration of which was as high as in the case of camphor itself. Attention may perhaps be directed to the large range of readings covered by Tables IV and VI, containing values for 39 and 32 wave-lengths, respectively, to the clearly-seen anomalies of Table V, and to the close concordance with the interpolation formula which is shown by the two long series of 33 readings in Table X.

TABLE V.

Rotations of α′-Bromocamphor in Benzene at 20°.

14·5020 G. of α′-bromocamphor in 100 g. of solution.
Density 0·92847. Length of tube 6 dcm.

$[\alpha] = 1{\cdot}238\alpha$. $[M] = 2{\cdot}311[\alpha]$.

$$[\alpha] = \frac{10{\cdot}232}{\lambda^2 - 0{\cdot}10630} - \frac{26{\cdot}393}{\lambda^2 - 0{\cdot}03525}.$$

(*a*) Visual Readings.

Wave-length.	Spec. rot. Obs.	Cal.	Diff.	
Li 6707·8	−33·6°	−33·9°	+0·3°	
Cd 6438·5	−36·2	−36·4	+0·2	
Zn 6362·3	−37·0	−37·1	+0·1	
Na 5893·0	−42·1	−42·1	±	
Hg 5780·1	−43·4	−43·4	±	
Cu 5782·2	−43·3	−43·4	+0·1	
Cu 5700·2	−44·3	−44·3	±	
Hg 5460·7	−47·0	−47·0	±	Inflection.
Cu 5218·2	−49·8	−49·7	−0·1	
Cu 5153·2	−50·5	−50·3	−0·2	
Cu 5105·5	−50·8	−50·8	±	
Cd 5085·8	−50·8	−51·0	+0·2	
Zn 4810·5	−52·7	−52·7	±	
Cd 4799·9	−52·7	−52·8	+0·1	
Zn 4722·2	−52·8	−52·9	+0·1	Maximum.

(*b*) Photographic Readings.

Fe 4256	*−43·3*	*−44·1*	*+0·8*	
Fe 4090	*−30·9*	*−32·1*	*+1·2*	
Fe 3953	*−12·4*	*−13·3*	*+0·9*	
Fe 3917	*− 6·2*	*− 6·2*	±	
Fe 3890	*0·00*	*− 0·1*	*−0·1*	*Reversal.*
Fe 3864	*+ 6·7*	*+ 6·6*	*+0·1*	
Fe 3841	*+12·4*	*+13·1*	*−0·7*	

Table VI.

Rotations of β-Bromocamphor in Benzene at 20°.

33·3710 G. of β-bromocamphor in 100 g. of solution.
Density 0·79569. Length of tube 6 dcm.

$[\alpha] = 0{\cdot}6277\alpha$. $[M] = 2{\cdot}311[\alpha]$. $[\alpha] = \frac{9{\cdot}7419}{\lambda^2 - 0{\cdot}09915} - \frac{8{\cdot}1869}{\lambda^2}$.

(*a*) Visual Readings.

Wave-length.	Spec. rot. Obs.	Cal.	Diff.
Li 6707·8	9·5°	9·6°	−0·1°
Cd 6438·5	11·1	10·5	+0·6
Zn 6362·3	11·7	11·7	±
Na 5893·0	15·7	15·7	±
Cu 5782·2	16·9	16·9	±
Hg 5780·1	17·0	17·0	±
Cu 5700·2	17·8	18·0	−0·2
Ag 5468·6	21·4	20·7	+0·7
Hg 5460·7	21·5	21·5	±
Cu 5218·2	26·1	26·2	−0·1
Ag 5209·1	26·2	26·4	−0·2
Cu 5153·3	27·8	27·7	+0·1
Cu 5105·5	29·1	28·9	+0·2
Cd 5085·8	29·4	29·4	±
Zn 4810·5	38·5	38·3	+0·2
Cd 4799·9	38·9	38·7	+0·2
Zn 4722·2	42·2	42·0	+0·2
Hg 4358·3	64·2	64·2	±

(*b*) Photographic Readings.

Wave-length.	Spec. rot. Obs.	Cal.	Diff.
Fe 5268	*25·2°*	*25·2°*	±
Fe 4825	*37·7*	*37·7*	±
Fe 4571	*50·2*	*49·6*	*+0·6°*
Fe 4384	*62·8*	*62·1*	*+0·7*
Fe 4424	*75·3*	*74·4*	*+0·9*
Fe 4144	*87·9*	*86·8*	*+1·1*
Fe 4054	*100·4*	*99·6*	*+0·8*
Fe 3990	*113·0*	*110·8*	*+2·2*
Fe 3926	*125·5*	*124·0*	*+1·5*
Fe 3874	*131·8*	*133·1*	*−1·3*
Fe 3825	*150·7*	*150·7*	±
Fe 3793	*163·2*	*159·7*	*+3·5*
Fe 3758	*175·8*	*179·0*	*−3·2*
Fe 3716	*188·3*	*191·0*	*−2·7*

Table VII.

Rotations of αα′-Dibromocamphor in Benzene at 20°.

17·4070 G. of αα′-dibromocamphor in 100 g. of solution.
Density 0·96100. Length of tube 6 dcm.

$[\alpha] = 0{\cdot}9963\alpha$. $[M] = 3{\cdot}100[\alpha]$. $[\alpha] = \frac{14{\cdot}666}{\lambda^2 - 0{\cdot}11296} - \frac{8{\cdot}1713}{\lambda^2}$.

(*a*) Visual Readings.

Wave-length.	Spec. rot. Obs.	Cal.	Diff.
Li 6707·8	25·6°	25·4°	+0·2°
Cd 6438·5	29·8	28·9	+0·9
Zn 6362·3	30·1	30·1	±
Na 5893·0	39·6	39·1	+0·5
Cu 5782·2	42·1	41·8	+0·3
Hg 5780·1	42·0	41·9	+0·1
Cu 5700·2	43·8	44·0	−0·2
Hg 5460·7	50·2	51·8	−1·6
Cu 5218·2	61·8	62·0	−0·2
Cu 5153·2	65·2	65·3	−0·1
Cu 5105·5	67·8	67·9	−0·1
Cu 5085·8	69·3	69·1	+0·2
Zn 4810·5	88·5	88·5	±
Cd 4799·9	88·9	88·7	+0·2
Hg 4358·3	149·0	147·5	+1·5

(*b*) Photographic Readings.

Wave-length.	Spec. rot. Obs.	Cal.	Diff.
Fe 4900	*79·7°*	*82·1°*	*−2·4°*
Fe 4690	*99·6*	*99·8*	*−0·2*
Fe 4555	*114·6*	*115·8*	*−1·2*
Fe 4426	*134·5*	*135·2*	*−0·7*
Fe 4328	*154·4*	*154·0*	*+0·4*
Fe 4178	*189·3*	*191·2*	*−1·9*
Fe 4120	*199·3*	*206·8*	*−7·5*
Fe 4046	*239·1*	*239·1*	±

TABLE VIII.

Rotations of αβ-Dibromocamphor in Benzene.

16·903 G. of αβ-dibromocamphor in 100 g. of solution.

Density 0·9602. Length of tube 6 dcm.

$[\alpha] = 1{\cdot}0269\alpha$. $[M] = 3{\cdot}101[\alpha]$. $[\alpha] = \frac{16{\cdot}134}{\lambda^2 - 0{\cdot}09863} + \frac{5{\cdot}8907}{\lambda^2}$.

(*a*) Visual Readings.

Wave-length.	Spec. rot. Obs.	Cal.	Diff.
Li 6707·8	+59·24°	+59·01°	+0·23°
Cd 6438·5	65·24	65·28	−0·04
Zn 6362·3	67·25	67·25	±
Na 5893·0	82·05	81·85	+0·20
Hg 5790·7	85·88	85·73	+0·15
Cu 5782·2	86·17	86·07	+0·10
Hg 5769·6	86·59	86·57	+0·02
Cu 5700·2	89·29	89·42	−0·13
Ag 5465·5	100·44	100·35	+0·09
Hg 5460·7	100·64	100·60	+0·04
Cu 5218·2	114·44	114·53	−0·09
Ag 5209·1	115·42	115·12	+0·30
Cu 5153·2	118·99	118·83	+0·16
Cu 5105·5	122·23	122·17	+0·06
Cd 5085·8	123·85	123·60	+0·25
Zn 4810·5	146·84	146·97	−0·13
Cd 4799·9	148·02	148·02	±
Zn 4722·2	156·05	156·16	−0·11
Zn 4680·1	160·88	160·88	±
Cd 4678·2	160·98	161·11	−0·13
Hg 4358·3	206·62	207·68	−1·06

(*b*) Photographic Readings.

Wave-length.	Spec. rot. Obs.	Cal.	Diff.
Fe 4655	*163·8°*	*163·9°*	*−0·1°*
Fe 4368	*205·2*	*205·9*	*−0·7*
Fe 4312	*215·4*	*216·5*	*−1·1*
Fe 4265	*225·6*	*226·1*	*−0·5*
Fe 4174	*245·8*	*247·3*	*−1·5*
Fe 4135	*256·0*	*257·5*	*−1·5*
Fe 3982	*307·5*	*306·4*	*+1·1*
Fe 3952	*317·8*	*318·1*	*−0·3*
Fe 3928	*328·1*	*328·1*	±
Fe 3883	*348·6*	*348·5*	*+0·1*
Fe 3811	*388·1*	*386·7*	*+1·4*
Fe 3795	*398·2*	*397·3*	*+0·9*

TABLE IX.

Rotations of α′β-Dibromocamphor in Benzene.

16·858 G. of α′β-dibromocamphor in 100 g. of solution.

Density 0·9573. Length of tube 6 dcm.

$[\alpha] = 1{\cdot}0327\alpha$. $[M] = 3{\cdot}101[\alpha]$. $[\alpha] = \frac{-\ 21{\cdot}4901\lambda^2 - 0{\cdot}509820}{\lambda^4 - 0{\cdot}047696\lambda^2 + 0{\cdot}008542}$.

Wave-length.	Spec. rot. Obs.	Cal.	Diff.
Li 6707·8	−53·68°	−53·70°	+0·02°
Cd 6438·5	58·64	58·64	±
Zn 6362·3	60·34	60·16	−0·18
Na 5893·0	70·68	70·82	+0·14
Hg 5790·7	73·31	73·49	+0·18
Cu 5782·2	73·70	73·65	+0·05
Hg 5769·6	73·98	74·06	+0·08
Cu 5700·2	76·06	75·97	−0·09
Ag 5471·6	82·81	82·77	−0·04
Hg 5460·7	83·11	83·11	±
Cu 5218·2	91·19	91·27	+0·08
Ag 5209·1	91·44	91·59	+0·15
Cu 5153·2	−93·42°	−93·63°	+0·21°
Cu 5105·5	95·47	95·41	−0·06
Cd 5085·8	95·91	96·16	+0·25
Zn 4810·5	107·39	107·39	±
Cd 4799·9	108·03	107·86	−0·17
Zn 4722·2	111·38	111·32	−0·06
Zn 4680·1	113·28	113·24	−0·04
Cd 4678·2	113·33	113·33	±
Fe 4448	*124·49*	*124·49*	±
Hg 4358·3	129·17	129·12	−0·05
Fe 4251	*134·81*	*134·85*	*+0·04*

TABLE X.

Rotations of απ- and α′π-Dibromocamphor in Benzene.

(*a*) 15·490 G. of απ-dibromocamphor in 100 g. of solution.

Density 0·9522. Length of tube 6 dcm.

$[\alpha] = 1{\cdot}1300a$. $[M] = 3{\cdot}101[\alpha]$.

$$[\alpha] = \frac{25{\cdot}163}{\lambda^2 - 0{\cdot}10476} - \frac{5{\cdot}741}{\lambda^2}.$$

(*b*) 6·204 G. of α′π-dibromocamphor in 100 g. of solution.

Density 0·9071. Length of tube 6 dcm.

$[\alpha] = 2{\cdot}9614a$. $[M] = 3{\cdot}101[\alpha.]$.

$$[\alpha] = \frac{34{\cdot}648}{\lambda^2 - 0{\cdot}10470} - \frac{15{\cdot}659}{\lambda^2}.$$

(*a*) Visual Readings.

Wave-length.	Spec. rot. Obs.	Cal.	Diff.	Spec. rot. Obs.	Cal.	Diff.
Li 6707·8	+60·67°	+60·13°	+0·54°	+66·00°	+65·56°	+0·44°
Cd 6438·5	67·38	67·38	±	74·06	74·06	±
Zn 6362·3	69·56	69·69	−0·13	76·82	76·78	+0·04
Na 5893·0	87·30	87·23	+0·07	98·11	97·75	+0·36
Hg 5790·7	91·99	92·02	−0·03	104·00	103·54	+0·46
Cu 5782·2	92·11	92·44	−0·33	104·33	104·05	+0·28
Hg 5769·6	92·91	93·06	−0·15	104·66	104·80	−0·14
Cu 5700·2	96·25	96·62	−0·37	109·39	109·14	+0·25
Ag 5468·6	110·39	110·51	−0·12	125·59	125·67	−0·08
Hg 5460·7	110·83	110·83	±	126·63	126·55	+0·08
Cu 5218·2	129·09	129·11	−0·02	148·93	149·22	−0·29
Ag 5209·1	130·01	129·89	+0·12	149·83	150·20	−0·37
Cu 5153·2	134·86	134·86	±	156·45	156·42	+0·03
Cu 5105·5	139·06	139·37	−0·31	162·11	162·09	+0·02
Cd 5085·8	141·69	141·30	−0·21	164·33	164·52	−0·19
Zn 4810·5	173·87	173·87	±	205·82	205·78	+0·04
Cd 4799·9	175·38	175·69	+1·19	208·13	207·70	+0·43
Zn 4722·2	187·20	187·08	+0·12	222·70	222·69	+0·01
Zn 4680·1	193·86	193·96	−0·10	231·58	231·54	+0·04
Cd 4678·2	194·34	194·32	+0·02	232·88	231·97	+0·91
Hg 4358·3	264·79	265·15	−0·36	323·53	323·99	−0·46

(*b*) Photographic Readings.

Wave-length.	Spec. rot. Obs.	Cal.	Diff.	Wave-length.	Spec. rot. Obs.	Cal.	Diff.
Fe 4294	*284·8°*	*284·9°*	*−0·1°*	*Fe 4368*	*319·9°*	*320·4°*	*−0·5°*
Fe 4280	*290·4*	*289·5*	*+0·9*	*Fe 4261*	*364·3*	*364·6*	*−0·3*
Fe 4261	*296·1*	*296·0*	*+0·1*	*Fe 4234*	*377·7*	*377·3*	*+0·4*
Fe 4122	*352·6*	*352·5*	*+0·1*	*Fe 4207*	*391·0*	*390·8*	*+0·2*
Fe 4076	*375·2*	*375·5*	*−0·3*	*Fe 4152*	*420·6*	*421·0*	*−0·4*
Fe 3927	*471·2*	*471·6*	*−0·4*	*Fe 4061*	*479·9*	*480·4*	*−0·5*
Fe 3900	*493·8*	*493·8*	±	*Fe 4022*	*509·5*	*510·4*	*−0·9*
Fe 3874	*516·4*	*517·0*	*−0·6*	*Fe 3986*	*540·3*	*540·9*	*−0·6*
Fe 3851	*539·0*	*539·2*	*−0·2*	*Fe 3955*	*570·0*	*569·8*	*+0·2*
Fe 3809	*584·2*	*584·5*	*−0·3*	*Fe 3926*	*599·6*	*599·4*	*+0·2*
Fe 3740	*674·6*	*675·5*	*−0·9*	*Fe 3899*	*629·2*	*629·2*	±
Fe 3726	*697·2*	*697·2*	±	*Fe 3874*	*658·8*	*659·2*	*−0·4*

6. *Summary.*

(*a*) Measurements have been made of the optical rotations, over a range of wave-lengths, of α- and α′-chlorocamphor, of α, α′-, and β-bromocamphor, and of five isomeric dibromocamphors. Attention is directed to certain regularities in the optical rotations of related

compounds, but the behaviour of the π-derivatives is shown to be altogether exceptional.

(*b*) In nine cases out of ten, the curves of rotatory dispersion are *complex but normal*, *i.e.*, the rotation increases progressively as the wave-length diminishes, giving rise to quasihyperbolic dispersion curves, which do not exhibit any obvious anomalies; the dispersion is, however, not simple, since it cannot be represented by a single term of Drude's equation.

(*c*) The dispersion can usually be represented by two terms of the Drude equation; but in the case of α′β-dibromocamphor (where all the rotations are negative) imaginary values are obtained for the constants in such an equation, showing that the dispersions are of still greater complexity.

(*d*) In the case of α′-bromocamphor the negative term predominates over the positive term in the visible region, but a reversal of sign is observed in the early ultra-violet region; the dispersion is therefore not merely complex but definitely *anomalous*. An inflection at 5455 Å.U., maximum at 4710 Å.U., and reversal of sign at 3890 Å.U. have all been observed experimentally.

We are indebted to the Department of Scientific and Industrial Research and to the Commissioners of the Exhibition of 1851 for maintenance grants to two of us during the period in which this research was carried out.

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[*Received, February 20th*, 1924.
Revised, March 30th, 1925.]

CLXXII.—*The Molecular Condition of Phenol in Benzene Solution.*

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IN the course of an investigation dealing with the influence of various substances on the solvent power of water (Philip and Bramley, J., 1915, **107**, 377) it was found that the distribution ratio of phenol between water and benzene at 20° was constant over the concentration range studied, *viz.*, up to about 2 grams of phenol per litre of the benzene phase. On the other hand, Rothmund and Wilsmore (*Z. physikal. Chem.*, 1902, **40**, 611), working at 25° and over the concentration range 5·6—50 grams of phenol per litre of the benzene phase, had obtained values of P (= concentration in aqueous phase/concentration in benzene phase) which fell off regularly with increasing concentration. Further work has now

confirmed both the constancy of P at low phenol concentrations and its variation at higher concentrations, the departure from constancy occurring when the amount of phenol per litre of the benzene layer has risen to about 2·8 grams. This constancy of P over a range of concentration is of some interest in connexion with the question of the molecular condition of phenol in benzene solution, as shown below.

Experimental.

Specially purified benzene and phenol were employed in the partition experiments, which were carried out at a constant temperature of 25° in the usual manner. The analytical procedure described in the earlier paper (*loc. cit.*) was tested and found satisfactory.

The results are set out in Table I, in which C_W and C_B represent grams of phenol per litre of the aqueous layer and the benzene layer respectively, whilst $P = C_W/C_B$.

Table I.

C_W	0·190	0·395	0·532	0·750	0·930	1·029	1·123
C_B	0·438	0·907	1·245	1·748	2·134	2·378	2·632
P	0·434	0·435	0·427	0·429	0·437	0·433	0·426
C_W	1·354	1·523	1·72	1·87	2·33	2·92	4·62
C_B	3·224	3·63	4·11	4·49	5·57	7·04	11·75
P	0·420	0·420	0·418	0·416	0·418	0·415	0·395
C_W	4·99	9·68	17·0	19·7	23·8		
C_B	12·50	27·4	60·7	77·3	112·7		
P	0·399	0·352	0·280	0·255	0·211		

The values of P obtained by Rothmund and Wilsmore, so far as they fall within the above range of concentration, are somewhat lower than the values recorded in Table I, but fit in generally with the figures there given.

Experiments were made also on the partition of phenol between sodium chloride solutions and benzene, and it appears that the change over from a constant value for P to a variable value occurs at about the same phenol concentration as in the absence of salt.

Discussion of Results.

The fact that the partition coefficient—variable at higher concentrations—becomes constant for values of C_B below about 2·8 proves that in the lowest concentration range the phenol in the benzene solution has reached a steady molecular condition. Since the molecular weight of phenol in water is approximately normal up to fairly high concentrations, the steady condition in question must be that corresponding with simple $C_6H_5{\cdot}OH$ molecules.

On a first consideration this conclusion may seem to be incon-

sistent with the cryoscopic measurements carried out by many workers. Auwers, for example (*Z. physikal. Chem.*, 1893, 12, 696), using the freezing-point method, found 145 for the molecular weight of phenol in a benzene solution containing 3 g. of phenol per 1000 g. of benzene, *i.e.*, roughly 2·6 g. per litre of benzene. Whilst, therefore, the partition measurements indicate simple phenol molecules at this concentration, the results of the cryoscopic determinations, as usually interpreted, indicate association to the extent of about 50%.

There appear to be only two possible explanations for this contradiction. First it might be suggested that the presence of water in the partition experiments affects the molecular condition of the phenol, but this explanation must be dismissed, for the depression of the freezing point of benzene caused by the addition of phenol is practically the same whether the benzene is dry or wet. Thus, for example, the depressions observed with solutions of four different concentrations were as follows: (*a*) in absence of water, 0·252°, 0·421°, 0·799°, 1·045°, (*b*) in presence of water, 0·230°, 0·412°, 0·777°, 1·053°.

Secondly, it might be that the high value deduced cryoscopically for the molecular weight of phenol in benzene is due, not to the association of the phenol, but to the separation of a solid solution instead of the pure solid solvent. As a matter of fact, Garelli has proved (*Z. physikal. Chem.*, 1896, **21**, 122) that a solid solution separates when a solution of phenol in benzene begins to freeze. This observation, which does not appear to be generally known, disposes of the contradiction referred to above, and although Garelli considers that association does occur to some extent, the partition experiments now recorded show that association is negligible when the phenol concentration is less than about 2·8 g. per litre of the benzene solution.

In any case it is clearly not permissible, unless with the appropriate corrections, to deduce from cryoscopic data the extent to which phenol is associated in benzene solution, as it undoubtedly is at the higher concentrations. For these cases, however, the degree of association may be calculated from the partition data recorded above, on the following assumptions, (1) that at the higher concentrations the distribution of the simple molecules remains the same as at the low concentrations, (2) that the phenol in the water layer remains in the condition of simple molecules, and (3) that in the more concentrated benzene solutions there is an equilibrium between single and double phenol molecules. It is clear that the figures thus obtained can be only approximate, for on the addition of much phenol the two layers are no longer strictly water and benzene.

In Table II the partition data for the four highest concentrations are set out, along with the values of c_1 and c_2, the calculated molar concentrations of the single and double phenol molecules, respectively, in the benzene phase. From these values of c_1 and c_2 the association factor, A (apparent molecular weight/formula weight), has been deduced for each of the four solutions by the formula $A = (c_1 + 2c_2)/(c_1 + c_2)$.

TABLE II.

C_W.	C_B.	c_1.	c_2.	A.	c_1^2/c_2.
9·68	27·4	0·24	0·026	1·10	2·21
17·0	60·7	0·42	0·114	1·21	1·55
19·7	77·3	0·49	0·17	1·26	1·44
23·8	112·7	0·59	0·31	1·34	1·14

The values of the association factor A just tabulated are lower than those involved in Bruni's figures for the true molecular weight of phenol in benzene, based on corrected cryoscopic data (*Gazzetta*, 1898, **28**, i, 251), but are fairly consistent with the corresponding figures calculated by Mameli from ebullioscopic measurements (*ibid.*, 1903, **33**, i, 469).

If in the more concentrated solutions there is an equilibrium between single and double molecules, represented by $(C_6H_5{\cdot}OH)_2 \rightleftharpoons 2C_6H_5{\cdot}OH$, then c_1^2/c_2 should be a constant. Actually, as shown in the table, the value of c_1^2/c_2 decreases as C_B increases, hence it is probable that in a concentrated solution of phenol in benzene there are triple molecules as well as double ones (compare Herz, *Ber.*, 1905, **38**, 1138).

IMPERIAL COLLEGE, LONDON, S.W.7. [*Received, April 2nd*, 1925.]

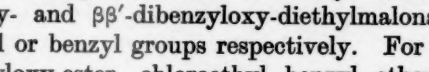
CLXXIII.—*Hepto- and Nono-dilactones.*

By GEORGE MACDONALD BENNETT.

THE *spiro*dilactones of ββ′-dihydroxy-diethyl- and -di-*n*-propyl-malonic acids (Leuchs and Gieseler, *Ber.*, 1912, **45**, 2114; Hjelt, *Annalen*, 1883, **216**, 67) are of particular interest in that they are among the simplest known substances which possess potential spiran asymmetry of the type recently realised by Mills and Nodder (J., 1921, **119**, 2094). A crystallographic examination of these two substances has now been made. They crystallise with trigonal and tetragonal symmetry, respectively. A resolution into the optically active forms by simple crystallisation has not been found possible: no enantiomorphism was detected in any crop of crystals obtained in many experiments with various solvents. The nono-

dilactone sometimes crystallises in pseudo-tetragonal form showing supplementary twinning of four biaxial individuals.

The methods of preparation of these two dilactones have been improved. The heptodilactone is easily formed from ethyl ββ′-dimethoxy- and ββ′-dibenzyloxy-diethylmalonate by removal of the methyl or benzyl groups respectively. For the preparation of the benzyloxy-ester, chloroethyl benzyl ether was required. This substance was isolated in an impure condition by Clemo and Perkin (J., 1922, **121**, 642), but has now been obtained pure by a convenient method and should prove to be a valuable synthetic reagent.

The δ-lactone formula  was assigned to the nonodilactone in Richter's "Chemie der Kohlenstoffverbindungen" (11th edn., 1909, p. 576), although the assumption made by Hjelt that his compound was the bis-γ-lactone was reasonable. The presence of the γ-lactone ring in a closely related bromo-compound was proved by Leuchs (*loc. cit.*), but direct evidence in the present case had not been produced. It is now shown that potassium hypobromite reacts at once with the dilactone, yielding bromoform. The presence of the group ·CH(OH)·CH_3 in the acid is therefore proved, and Hjelt's formula is confirmed.

Experimental.

Dilactone of ββ′-Dihydroxydiethylmalonic Acid.—Small yields (5—10%) of this substance were isolated from the products of interaction of ethyl malonate with sodium ethoxide and ethylene chlorohydrin, ethylene bromohydrin, chloroethyl acetate, bromoethyl acetate or chloroethyl *p*-nitrobenzoate (2 mols.) in ethyl-alcoholic solution. Ethyl acetate and ethyl *p*-nitrobenzoate were obtained in good yield in the last two cases, the latter being identified by direct comparison and by the melting point of a mixture with an authentic specimen. The appearance of ring closure by elimination of a molecule of ethyl acetate or ethyl *p*-nitrobenzoate would be remarkable: these substances may, however, have been formed in the alcoholic solution before the condensation occurred.

The dilactone was obtained in poor yield by the action of ethylene chlorohydrin (1 mol.) upon the sodium derivative of ethyl butyrolactonecarboxylate in alcoholic solution (Traube, *Ber.*, 1901, **34**, 1971), and by the use, under similar conditions, of ethylene oxide (2 mols.).* The heptodilactone was also produced in small quantity by the action of an alcoholic solution of sodium ethoxide upon *di-β-chloroethyl malonate*, a colourless liquid, b. p. 164°/15 mm.

* I am indebted to Dr. W. H. Mills, F.R.S., for this suggestion.

(Found: Cl, 30·5. $C_7H_{10}O_4Cl_2$ requires Cl, 31·0%), prepared from malonyl chloride and ethylene chlorohydrin.

Methyl Iodoethyl Ether.—The method of preparation described by Clarke (J., 1912, **101**, 1806) gives but a poor yield and is inconvenient unless an autoclave is used. The replacement of the hydroxyl group of glycol monomethyl ether by means of phosphorus tri-iodide was examined, as a similar reaction had been described for the corresponding ethyl ether by Demole (*Ber.*, 1876, **9**, 746), but the yield of the product was surprisingly low (10%) in spite of repeated experiments and considerable care in the exclusion of moisture and in the purification of the methyl glycol used. The unsatisfactory yield in the preparation of methyl iodoethyl ether makes the isolation of the heptodilactone depending on its use as described below, of little practical value.

Ethyl ββ'-Dimethoxydiethylmalonate.—The crude ester prepared in the usual manner from ethyl malonate and methyl iodoethyl ether (2 mols.) was purified by treatment with potassium hydroxide solution (compare Michael, *J. pr. Chem.*, 1905, **72**, 537). It is a colourless liquid, b. p. 153°/16 mm. (Found: C, 56·4; H, 8·8. $C_{13}H_{24}O_6$ requires C, 56·5; H, 8·8%). It is converted into heptodilactone by boiling for 10 minutes with concentrated hydriodic acid (5 parts), the solution being then diluted, neutralised, boiled for 15 minutes, and again acidified. The dilactone crystallises on cooling (yield 40%).

Benzyl β-Hydroxyethyl Ether.—To an excess of glycol (300 g.) a solution of sodium (37·5 g.) in ethyl alcohol (300 g.) was added and the alcohol distilled off, the last traces being removed by heating at 150° under diminished pressure. Benzyl chloride (225 g.) was gradually added, the reaction being allowed to subside after each addition, and the mixture was heated at 150° for 15 minutes. The oil and sodium chloride were separated by addition of acetone and filtration. The acetone was removed and the greater portion of the glycol recovered by distillation, after which the residue was washed with water, removed in ether, dried over potassium carbonate, and distilled (yield 166 g.).

Benzyl hydroxyethyl ether is a colourless oil, b. p. 138°/15 mm., not miscible with water, but soluble in alcohol and ether (Found: C, 71·0; H, 8·0. $C_9H_{12}O_2$ requires C, 71·1; H, 7·9%).

Action of Phosphorus Halides on Benzyl Hydroxyethyl Ether.—When the replacement of the hydroxyl group in the above compound was attempted by means of phosphorus trihalides, unexpected difficulties were encountered as in the case of the corresponding methyl ether. Thus, when benzyl hydroxyethyl ether (40 g.) reacted with phosphorus tribromide (1/3 mol.) in dry benzene

solution, only 15 g. were obtained of an oil of b. p. 120—130°/20 mm. which contained the desired benzyl bromoethyl ether together with some benzyl bromide, whilst a large residue of non-volatile phosphorus ester remained in the distillation flask. The use of phosphorus tri-iodide led in the same way to the isolation of a large proportion of crystalline benzyl iodide (identified by direct comparison with a pure specimen) and a small fraction which may have contained the iodoethyl ether but was insufficient for its complete isolation.

By means of a reaction described by Darzens (*Compt. rend.*, 1911, **152**, 1314), which has found little application until recently (*e.g.*, Helferich, *Ber.*, 1921, **54**, 1082), an almost quantitative conversion of the hydroxy-compound into its chloro-derivative is obtained by a rapid process.

Benzyl Chloroethyl Ether.—The liquid, prepared as described by Clemo and Perkin (*loc. cit.*), was a mixture of the chloroethyl ether with unchanged benzyl alcohol which could not easily be separated.

The pure substance was readily obtained as follows: A mixture of benzyl hydroxyethyl ether (16 g.) with dimethylaniline (13 g.) was treated below 30° with thionyl chloride (14·5 g.) dissolved in chloroform (10 c.c.). The whole was heated on the water-bath for ½ hour and then poured into dilute hydrochloric acid, the oil separated in chloroform, the extract washed successively with dilute acid and water, and distilled. *Benzyl chloroethyl ether* was thus obtained (13 g.) as an almost colourless oil of pleasant odour, b. p. 124°/20 mm., $d_4^{20°}$ 1·109, $n_D^{20°}$ 1·5204 (Found: Cl, 20·65. $C_9H_{11}OCl$ requires Cl, 20·8%).

ββ′-Dibenzyloxydiethylmalonic Acid, $(C_7H_7{\cdot}O{\cdot}CH_2{\cdot}CH_2)_2C(CO_2H)_2$. —Ethyl malonate was heated for two successive periods of 8 hours at 100° in alcoholic solution with two quantities of sodium (1 equiv.) and benzyl chloroethyl ether (1 equiv.). The crude ester was extracted with potassium hydroxide solution, and hydrolysed by heating with alcoholic potassium hydroxide solution for 6 hours. The *acid*, isolated as a syrup which slowly solidified, crystallised from benzene–light petroleum in bundles of minute needles, m. p. 120° (Found: C, 67·6; H, 6·6. $C_{21}H_{24}O_6$ requires C, 67·7; H, 6·5%). It gives a sparingly soluble *calcium* salt and a *silver* salt (Found: Ag, 36·6. $C_{21}H_{22}O_6Ag_2$ requires Ag, 36·8%).

The crude ester was converted into the heptodilactone (yield 45—50%) by treatment with fuming hydrobromic acid in the cold for several days with frequent shaking. The benzyl bromide was removed in steam, the residue boiled with sodium hydroxide, and then cooled and extracted once with ether. The aqueous solution was concentrated and acidified, and the lactone crystallised on

cooling; m. p. 110° (Found: C, 53·8; H, 5·2. Calc., C, 53·8; H, 5·1%).

Dilactone of Dihydroxydipropylmalonic Acid.—Ethyl diallylmalonate (1 vol.) mixed with sulphuric acid (3 vols.: 70% by weight) was boiled for 3 minutes, diluted with an equal volume of water, and cooled. The dilactone thus obtained was pure after one crystallisation from water; m. p. 106° (Found: C, 58·6; H, 6·55. Calc., C, 58·7; H, 6·5%).

An examination of the mother-liquors in this preparation did not reveal the presence of any other crystalline substance, although three isomerides are conceivable, as with the dibromodilactones of Leuchs and Gieseler (*loc. cit.*).

Action of Potassium Hypobromite on the Nonodilactone.—A mixture of potassium hypobromite solution (8 mols.) with a solution of the pure nonodilactone in potassium hydroxide (2 mols.), when warmed, became turbid and bromoform settled as a heavy oil of b. p. 151°, giving the carbylamine reaction with aniline and sodium hydroxide solution.

Crystallographic Properties of the Dilactones.

Heptodilactone (Bis-γ-butyrolactone-αα-spiran).—The substance crystallises magnificently from acetone, benzene, or water in trigonal crystals having the Millerian axial angle of 127° 18′ (Bravais-Miller axial ratio $a : c = 1 : 2{\cdot}902$). Forms observed: $c\{111\}$ and $r\{100\}$, the crystals being tabular with c large. Measurements of four selected crystals gave the mean angular values: cr 73° 23′, rr 112° 15′ (calc. 112° 10′). No marked cleavage was observed. The crystals are uniaxial with positive double refraction. Density (by suspension in dense liquids, corr.) $D_4^{15°}$ 1·541. Refractive indices (D line, by immersion in oils) $\omega = 1{\cdot}552$, $\epsilon = 1{\cdot}588$.

Nonodilactone (Bis-γ-valerolactone-αα-spiran).—This substance has previously been described (Hjelt, *loc. cit.*) as orthorhombic with $a : b : c = 0{\cdot}61 : 1 : 0{\cdot}94$, but the crystals examined were imperfectly developed and only two angles were recorded, measured to the nearest 30′.

In the present investigation well-formed crystals were obtained from solutions in acetone, ethyl alcohol, or ethyl acetate. They are tetragonal, with axial ratios $a : c = 1 : 1{\cdot}710$. Forms observed: $c\{001\}$, $r\{101\}$, $s\{201\}$ and sometimes $m\{110\}$. Large crystals from acetone showed the above forms equally developed, while crystals from ethyl acetate and ethyl alcohol were tabular with forms c and s only, c being large. Measurements from six crystals gave the mean angular values: cr 59° 41′, cs 73° 37′ (73° 42′), ss 85° 30′ (85° 29′) (calculated values in brackets). Crystals from water

sometimes showed the combination *r*, *s* and *m*. Possibly this was the combination observed by Hjelt, the face he refers to as *c* being (110). An imperfect cleavage was noticed parallel to *a* {100}.

Large tabular crystals were usually found to be uniaxial with strong positive double refraction. Density $D_4^{15°}$ 1·321. Refractive indices: $\omega = 1{\cdot}494$, $\epsilon = 1{\cdot}571$.

The statement in Hjelt's description that the substance was optically biaxial was accounted for when many small tabular crystals were observed to be twins of four biaxial individuals having a straight extinction and arranged with the acute bisectrix of positive double refraction emerging perpendicular to the basal plane. No sign of the complexity of the whole was detected by examination in ordinary light. Measurements of the optic axial angle (crystals immersed in oil of $n = 1{\cdot}494$) gave results varying from 8° to 15°, doubtless owing to the difficulty of ensuring the passage of the converging beam of light through one individual alone of so small a complex crystal. It appears improbable that the optical properties of these crystals are the result merely of strain in growth, yet the observation of Martin (*Neues Jahrb. Min.*, 1891, **7**, 1) in a similar case, that minute crystals as first deposited from solution were uniaxial, has been confirmed with this substance.

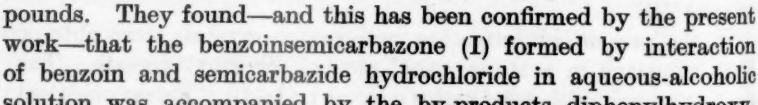
My thanks are due to Miss E. M. Whincop for help with some of the experiments above described, and to the Chemical Society for assistance in the purchase of materials.

THE UNIVERSITY, SHEFFIELD. [*Received, March 6th*, 1925.]

CLXXIV.—*Semicarbazones of Benzoin. Part I.*

By ISAAC VANCE HOPPER.

BILTZ and his co-workers (*Annalen*, 1905, **339**, 243) have examined the action of semicarbazide on benzoin, benzil, and related compounds. They found—and this has been confirmed by the present work—that the benzoinsemicarbazone (I) formed by interaction of benzoin and semicarbazide hydrochloride in aqueous-alcoholic solution was accompanied by the by-products diphenylhydroxytriazine (II; keto-form) and diphenyliminazolone (III).



Biltz proved that oxidation of a part of the benzoin or benzoinsemi-

carbazone to benzil or benzilsemicarbazone, followed by loss of water from the last-mentioned compound through intramolecular condensation, gave rise to (II), but his explanation of the mechanism of this oxidation and of the formation of (III) is unsatisfactory.

The presence of ammonia in the spent liquors and of (II) and (III) as by-products (see also Biltz, *loc. cit.*) suggests to the author that benzoin can react with semicarbazide after the fashion of α-hydroxy-ketones and phenylhydrazine, yielding a derivative of the corresponding diketone, the oxidation of the secondary alcoholic group being effected by semicarbazide, which is thereby reduced to ammonia and carbamide, the latter of which condenses with unchanged benzoin (acting as αβ-dihydroxystilbene) to form diphenyliminazolone :

$$(I) + NH_2{\cdot}NH{\cdot}CO{\cdot}NH_2 \rightarrow (IV) + NH_3 + (NH_2)_2CO;$$

$$(IV) \rightarrow (II) + H_2O; \quad PhCH(OH){\cdot}COPh \rightleftharpoons PhC(OH){:}C(OH)Ph \xrightarrow{CO(NH_2)_2} (III) + 2H_2O.$$

Benzoin has been condensed with carbamide in alcoholic solution (Anschutz, *Annalen*, 1891, **261**, 129; 1894, **284**, 8) and in acetic acid solution (Biltz and Stellbaum, *ibid.*, 1905, **339**, 264) to give good yields of diphenyliminazolone. Incidentally there is strong evidence here that benzoin can behave in a dienolic form. The formation of (II) precludes the formation of benzildisemicarbazone and also accounts for the absence of benzilmonosemicarbazone from the reaction products.

Benzoin and δ-benzylsemicarbazide hydrochloride in aqueous-alcoholic solution reacted in a similar manner. In this case, however, the presence of the benzyl radicle in the δ-position of the semicarbazide residue inhibited hydroxytriazine formation, and the chief product of the reaction was benzildibenzylsemicarbazone (VII); a little benzilmonobenzylsemicarbazone (VI) and varying amounts of benzoinbenzylsemicarbazone (V) were also obtained.

$$\underset{\text{(V.)}}{\begin{matrix}PhCH{\cdot}OH\\ PhC{:}N{\cdot}NH{\cdot}A\end{matrix}} \xrightarrow{NH_2{\cdot}NH{\cdot}A} \underset{\text{(VI.)}}{\begin{matrix}PhCO\\ PhC{:}N{\cdot}NH{\cdot}A\end{matrix}} \xrightarrow{NH_2{\cdot}NH{\cdot}A} \underset{\text{(VII.)}}{\begin{matrix}PhC{:}N{\cdot}NH{\cdot}A\\ PhC{:}N{\cdot}NH{\cdot}A\end{matrix}}$$

$$[A = CO{\cdot}NH{\cdot}CH_2Ph]$$

In conformity with the foregoing interpretation, benzoin-δ-benzylsemicarbazone (1 mol.) and δ-benzylsemicarbazide hydrochloride (2 mols.) reacted in alcoholic solution to give benzildi-δ-benzylsemicarbazone (1 mol.), which, being practically insoluble, separated almost quantitatively. δ-Phenylsemicarbazide gave similar results.

Biltz's statement " Das Diphenylimidazolon ist andererseits aus Benzoinsemicarbazone unter Austritt der Bestandteile von Hydroxylamine entstanden zu denken : $C_{15}H_{15}O_2N_3 = H_3NO + C_{15}H_{12}ON_2$ "

has no experimental foundation whatsoever. To depict such a change would require an unusual interchange of atoms and bonds. Benzoin and δ-benzylsemicarbazide hydrochloride interact to give the mono- and di-δ-benzylsemicarbazones of benzil, but no iminazolone, and hence no benzylhydroxylamine, is formed. This renders untenable Biltz's view that the oxidation of benzoin or benzoinsemicarbazone is occasioned by hydroxylamine.

Whilst benzoin-δ-benzylsemicarbazone is stable in alcohol, an alcoholic solution containing a few drops of hydrochloric acid gave, after some days, benzildi-δ-benzylsemicarbazone. This conversion must be due, in the first instance, to hydrolysis of at least a portion of the benzoin derivative, since otherwise there would be no free hydrazide to combine with the ketonic group formed in the oxidation. This influence of hydrochloric acid is also evinced by the fact that a dilute aqueous-alcoholic solution of benzoin and δ-benzylsemicarbazide hydrochloride gave less benzildi-δ-benzylsemicarbazone and more benzoin-δ-benzylsemicarbazone than did a more concentrated solution of the same reactants. The oxidation of the :CH·OH group would therefore seem to be dependent on the acid in the semicarbazide hydrochloride employed, a conclusion supported by the absence of benzil derivatives when benzoin and semicarbazides (as hydrochlorides) condense in pyridine solution.

The condensation of benzoin with semicarbazides in pyridine solution, in addition to opening up a new method of semicarbazone formation which will be extended, gave excellent yields of the semicarbazones. In three cases, tabulated below, isomerides were obtained.

M. p. of	α-Form.		β-Form.	
Semicarbazone	206°		187°	
δ-Phenylsemicarbazone	198		169	
δ-Benzylsemicarbazone		115°		
δα-Phenylethylsemicarbazone *	174		154	137° (γ-form)

* Unpublished work.

Excepting the last-mentioned instance, the yield of β-isomeride was comparatively small. The benzylsemicarbazone, of which only one form was isolated after recrystallisation from various solvents, would seem from its low melting point to be a mixture. The higher-melting modification of the stereoisomeric semicarbazones is termed the α-isomeride; this is in accordance with the practice adopted by Wilson (J., 1912, **101**, 1482; 1913, **103**, 377, 1504), Wallach (*Ber.*, 1898, **28**, 1955), and Forster (J., 1910, **97**, 2156).

According to Biltz (*loc. cit.*), who evidently carried out the operation in aqueous solution, when benzoinsemicarbazone is heated

with hydrochloric acid, hydrolysis to benzoin and semicarbazide is immediately followed by reduction of the ketone to hydrobenzoin. The author has found, however, that benzoinsemicarbazone (α-form), like all the semicarbazones described in this paper, when heated with alcohol and hydrochloric acid for a short time is quickly hydrolysed, giving benzoin.

EXPERIMENTAL.

Benzoinsemicarbazone.—Solutions of 8·5 g. (1 mol.) of recrystallised semicarbazide hydrochloride in 20 c.c. of water and of 16 g. (1 mol.) of benzoin in 160 g. of pyridine were mixed in the cold, kept for 6 days, and poured into 2400 c.c. of cold water. The precipitate, collected after an hour and recrystallised from alcohol, consisted almost entirely of benzoinsemicarbazone (α-form: m. p. 205—206°), previously described by Biltz. The aqueous pyridine filtrate, diluted to 3500 c.c. and left over-night, deposited a second crop which, although much more soluble in alcohol, gave from this solvent, after standing over-night, a proportion of the α-isomeride which was collected. The alcoholic filtrate usually contained a little more of this modification, which was removed by careful treatment involving evaporation, addition of cold alcohol to the mother-liquor in contact with the separated product, and collection of the undissolved portion; this treatment was repeated until small, almost cubical, crystals of the β-*isomeride* appeared and grew as the solution evaporated to small bulk. The final mother-liquor, diluted with water to incipient cloudiness and decolorised with neutral animal charcoal, gave a little more of the β-compound, the whole of which was recrystallised twice from alcohol, giving colourless, almost cubical crystals not changed by further recrystallisation; m. p. 186—187° (decomp.) (Found: N, 15·7; *M*, ebullioscopic in alcohol, 279. $C_{15}H_{15}O_2N_3$ requires N, 15·6%; *M*, 269). The β-isomeride, which is moderately soluble in boiling benzene or boiling ether and insoluble in water, differs greatly from the α-modification in solubility and crystalline form. A mixture of both forms melts at 179—200°.

Hydrolysis.—Both forms, when separately dissolved in alcohol and boiled for a minute or two with concentrated hydrochloric acid, gave, on cooling and dilution with water, crystals of benzoin which, after recrystallisation from alcohol, were identified by physical tests and by conversion into benzoin benzoate, m. p. 124° (Wren, J., 1909, **95**, 1601, gives m. p. 124—125°). Hydrobenzoin mono- and di-benzoates melt at 160° and 247°, respectively.

Benzildi-δ-benzylsemicarbazone.—This compound was slowly formed in good yield as a crystalline precipitate when solutions

of 4 g. (1 mol.) of δ-benzylsemicarbazide hydrochloride in 8 c.c. of water and of 4 g. (1 mol.) of benzoin in 75 c.c. of alcohol were mixed and kept 4—5 days at room temperature. The action may be hastened by warming. When separation of this disemicarbazone had ceased, the mother-liquor, by evaporation or by dilution with water, gave three products, *viz.*, a little more benzildi-δ-benzylsemicarbazone, some benzilmono-δ-benzylsemicarbazone, and about 1·5 g. of benzoin; the first of these, being almost insoluble in boiling 90% alcohol, and the second, being moderately soluble in the cold, were easily separated from benzoin by treatment with this solvent. The final mother-liquor gave a viscous product which did not solidify. *Benzilmono-δ-benzylsemicarbazone*, obtained in small quantity as six-sided plates, m. p. 198°, was hydrolysed to benzil by boiling alcohol and hydrochloric acid (Found: N, 11·5. $C_{22}H_{19}O_2N_3$ requires N, 11·8%). The *dibenzylsemicarbazone*, irregular, minute scales (m. p. 239—240°) from glacial acetic acid–alcohol, was identified by comparison with an authentic specimen, and by hydrolysis to benzil by heating for ½ hour with a mixture of glacial acetic and hydrochloric acids. It is insoluble in water, ether, or light petroleum, almost insoluble in alcohol or benzene, and is unchanged by short boiling with caustic soda or hydrochloric acid (Found: N, 16·55. $C_{30}H_{28}O_2N_6$ requires N, 16·7%).

The same compound was formed when 1 g. (1 mol.) of benzoin-δ-benzylsemicarbazone in 10 c.c. of alcohol was heated at 60° for a few hours with 1·1 g. (2 mols.) of δ-benzylsemicarbazide hydrochloride in 2 c.c. of water, and also when a mixture of benzil (1 g.) in hot alcohol (10 c.c.) with excess of δ-benzylsemicarbazide hydrochloride (5·8 g.) in alcohol (20 c.c.) was heated to boiling for 15 minutes and then at 60° for some hours. In both cases the product was collected after 12 hours and purified as above, the yield being nearly theoretical.

Benzoin-δ-benzylsemicarbazone.—Alcoholic method.—Solutions of 4 g. (1 mol.) of δ-benzylsemicarbazide hydrochloride in 8 c.c. of water and of 4 g. (1 mol.) of benzoin in 130 c.c. (nearly double the previous amount) of alcohol were mixed and left for 9 days at the ordinary temperature until separation of benzildi-δ-benzylsemicarbazone had ceased. Water (40 c.c.), added to the filtrate, precipitated the remainder of this compound and a little benzoin, which were collected. In an hour or so, the filtrate began to deposit crystals of benzoin-δ-benzylsemicarbazone, the separation of which was, after some time, rendered complete by the addition of water. The yield (about 5 g.) of benzoin derivative is attributed to the large amount of alcohol used.

Pyridine method.—Cold solutions of 5 g. (1. mol) of δ-benzylsemi-

carbazide hydrochloride in 5 c.c. of water and of 5 g. (1 mol.) of benzoin in 50 c.c. of pyridine were mixed and left for 5 days at room temperature. The mixture was then diluted with 100 c.c. of water and poured into 2 litres of well-stirred cold water. The precipitated semicarbazone, when collected and recrystallised twice from alcohol, gave long, fine needles, m. p. 115°, which were unchanged by recrystallisation from other solvents.

Benzoin-δ-benzylsemicarbazone is easily soluble in chloroform or alcohol, less soluble in ether or benzene, and insoluble in light petroleum or water, and in alcoholic solution is hydrolysed by hydrochloric acid to benzoin and δ-benzylsemicarbazide hydrochloride. Yield: 90% (Found: N, 11·5. $C_{22}H_{21}O_2N_3$ requires N, 11·6%).

Benzoin-δ-phenylsemicarbazone.—Alcoholic method: α-Form.—When 4 g. (1 mol.) of δ-phenylsemicarbazide hydrochloride dissolved in 8 c.c. of water were added to a solution at 45° of 4 g. (1 mol.) of benzoin in 130 c.c. of alcohol, and the mixture was kept at room temperature, separation of the *phenylsemicarbazone* (α-form) began after 18 hours and continued for 2 days. Water added to the filtrate precipitated a little more of the product. Recrystallisation from alcohol, in which it was difficultly soluble, gave a woolly mass of fine needles, m. p. 198° (decomp.) (Found: N, 12·2. $C_{21}H_{19}O_2N_3$ requires N, 12·2%). The almost theoretical yield is partly attributed to the sparing solubility of the compound causing separation before oxidation to a benzil derivative can take place. The compound should prove useful for the identification of small quantities of benzoin, into which it is hydrolysed by heating with alcohol and hydrochloric acid.

Pyridine method: α- and β-Forms.—When 5 g. of δ-phenylsemicarbazide were added to a cold solution of 6·5 g. of benzoin in 45 c.c. of pyridine, complete solution took place. The mixture, after standing 6 days at room temperature, was diluted with water to incipient cloudiness and kept over-night; the precipitate was collected and the filtrate treated with water as before. Next day, the second crop was collected, and this completed the separation of the α-isomeride, which was purified as previously described. Further addition of water to the pyridine liquor precipitated an emulsion which absorbed much colouring matter from the solution and solidified later as small hard spheres; these were collected, washed, and dried. Decoloration, although difficult, was effected by diluting an ethereal solution with light petroleum to incipient cloudiness and boiling with animal charcoal. The filtrate slowly deposited hard, stout prisms which, when sifted from a little of the α-isomeride and recrystallised from the minimum of alcohol by spontaneous evaporation, gave clusters of needles, m. p. 169°. The

β-*isomeride*, unlike the α-form, is easily soluble in alcohol, moderately soluble in ether or benzene, insoluble in water or petroleum; on heating with alcohol and hydrochloric acid, it yields benzoin; and when mixed with the α-form, it melts at 160–165° (Found: N, 12·3%).

[With MAGNUS HERD.] *Benzildi-δ-phenylsemicarbazone.*—One gram of benzil in 10 c.c. of hot alcohol was heated under reflux with 2·8 g. (excess) of δ-phenylsemicarbazide hydrochloride in a little hot water for 3 hours. After 12 hours, the product was collected and recrystallised twice from glacial acetic acid, separating in rhombic plates, m. p. 253° (decomp.) (70% yield), moderately soluble in alcohol, insoluble in water (Found: N, 17·8. $C_{28}H_{24}O_2N_6$ requires N, 17·6%). The same compound was formed when a mixture of 1 g. (1 mol.) of benzoin-δ-phenylsemicarbazone in 20 c.c. of alcohol with 1·2 g. (2 mols.) of δ-phenylsemicarbazide hydrochloride in a little water was heated under reflux for 2 hours. After concentrating and keeping, the product was purified as before. It was also obtained when a mixture of 2 g. (1 mol.) of benzoin in 20 c.c. of hot alcohol with 5·5 g. (3 mols.) of δ-phenylsemicarbazide hydrochloride in 4 c.c. of water was heated under reflux for 3 hours, the product being worked up as in the last-mentioned instance.

I am much indebted to Professor F. J. Wilson, who introduced me to this work, and to Dr. W. M. Cumming for their helpful interest. The expense of this research was partly met by a grant—now gratefully acknowledged—from the Carnegie Trustees.

THE ROYAL TECHNICAL COLLEGE,
GLASGOW.

[*Received, February 14th*, 1925.]

CLXXV.—*The Composition of Starch Iodide.*

By HUMPHREY DESMOND MURRAY.

THE composition of the blue compound produced by the reaction of iodine with starch in the presence of iodides has been the subject of numerous investigations, which have led to somewhat indefinite results (Mylius, *Ber.*, 1887, **20**, 688; Andrews and Goettsch, *J. Amer. Chem. Soc.*, 1902, **24**, 865; Harrison, P., 1910, **26**, 252; Barger and others, J., 1912, **101**, 1394; 1915, **107**, 411; 1924, **125**, 2407). According to Mylius, the blue compound formed in the presence of hydriodic acid has the composition $(C_{24}H_{40}O_{20}I)_4,HI$, and in dilute solution in presence of excess of iodide changes to a purplish-red compound; the ratio of iodine to hydrogen iodide is 4 : 1 for the blue compound and 2 : 1 for the red. Other inves-

tigators, however, have found the iodine content to vary within wide limits and have therefore concluded that an adsorption compound of iodine with starch is formed.

Iodine also forms blue compounds with other organic substances, many of which have been investigated by Barger and his associates. In the case of cholalic acid these workers found, for the mixed crystals formed in the presence of large iodine concentrations, a formula which corresponds more or less with that of Mylius given above, *viz.*, $(C_{24}H_{40}O_5I)_4,KI$.

The object of the present investigation was to determine the composition of the so-called starch iodide by examining the concentrations of free and combined iodine in the resultant solution when iodine dissolved in carbon tetrachloride is shaken with a solution of starch containing a known amount of potassium iodide. In order to calculate the concentration of the tri-iodide ion, the equilibrium concentration of the iodide ion was measured by means of an iodine electrode. Such determinations are most significant in solutions containing small concentrations of potassium iodide, and for precise measurements, therefore, it is necesssary to take into account the hydrolysis of iodine. In order to utilise the results of determinations of this hydrolysis in acid solution (this vol., p. 882), the present measurements were carried out in the presence of acid of the same concentration.

The iodine used was sublimed several times without the addition of potassium iodide. The starch solution was prepared from maize starch. This (10 g.) was shaken with 200 c.c. of 0·0001*N*-sulphuric acid, allowed to settle for some hours, washed with water by decantation over a period of 3 days, and dried first at 50° and finally at 110°. A solution of 2·5 g. of the starch powder in 500 c.c. of *N*/10-sulphuric acid was boiled for 1 minute, kept for 12 hours, and decanted from the small cellulose residue. Each series of measurements was made with the same solution, and was completed within 48 hours of the final decantation. Maize starch was chosen for the reason that its solution gives a precipitate less easily than that from potato starch and leaves less residue after boiling than those from the samples of wheat and rice starch obtainable.

When iodine dissolved in dilute potassium iodide solution is added to a solution of starch, a definite threshold concentration of the iodine is necessary before the blue colour appears. This necessitates a correction when dilute iodine solutions, such as were used in the present experiments, are being titrated. Treadwell ("Analytical Chemistry," 4th ed., Vol. II, p. 653) has pointed out that the amount of iodine solution which must be added to a starch solution to produce a blue coloration is directly proportional

to the volume of the starch solution. This result was confirmed, and with concentrations of starch and potassium iodide varying over fairly wide ranges, the iodine threshold concentration was found to have a constant value of $0{\cdot}15 \times 10^{-5}$ mol./litre (Meineke, *Chem. Ztg.*, 1894, **18**, 157).

Carbon tetrachloride free from sulphur was dried over calcium chloride and distilled while the temperature was constant. The requisite quantity of iodine was then dissolved in it, and the solution shaken with small quantities of water to remove any iodides which might have been formed. This course was shown to be necessary by preliminary experiments.

The procedure adopted throughout the measurements was as follows: In a thermostat at 25°, 10 c.c. of a solution of iodine in carbon tetrachloride were added to 25 c.c. of acid starch solution (and, in the later experiments, a certain volume of a solution of potassium iodide in N/10-sulphuric acid) and a sufficient quantity of N/10-sulphuric acid to bring the volume of the aqueous layer to 100 c.c. The whole was then shaken. When equilibrium had been established, 50 c.c. of the aqueous layer were poured into the electrode vessel, and the remainder was titrated against thiosulphate solution, which was repeatedly standardised. The solutions were not exposed to direct sunlight, and it was shown by preliminary experiments that measurable oxidation of very dilute potassium iodide solutions such as were used in the experiments does not take place. The electrodes were of platinum slightly coated with platinum black. The cell set up was:

$$\text{Pt. } I_2 | \text{Starch} + \text{KI} + N/10\text{-}H_2SO_4 | N/10\text{-}H_2SO_4 | Hg_2SO_4 . \text{Hg}.$$

The fact that iodine in sufficiently high concentration produces a blue coloration in a starch solution in absence of potassium iodide has been attributed to the formation of iodide ions through reduction of the iodine by the starch. A sufficient concentration of iodide ions to form the blue compound, however, might be produced by hydrolysis of the iodine alone. Measurements made to test this point showed that iodine was reduced to a slight extent by some substance in the starch, and that the reduction was proportional to the quantity of starch present. The concentration of iodide ions produced by reduction ($= B$) as opposed to the concentration of the latter due to hydrolysis was calculated as follows:

$$[I'][I^\cdot]/[I_2] = K_1; \quad [I'][I_2]/[I_3'] = K_2; \quad B = [I'] + [I_3'] - [I^\cdot];$$

where $[I_2]$ is the concentration of free iodine calculated from the distribution coefficient of iodine between carbon tetrachloride and N/10-sulphuric acid, $[I']$ is the concentration of the iodide ion

measured by the iodine electrode, $[I_3']$ is the concentration of the tri-iodide ion calculated from the equilibrium expression, and $[I^\cdot]$ is the concentration of positive iodine ions, the existence of which was assumed in determining the value of K_1.

In Table I is shown the value of B for a starch solution which had been shaken with a solution of iodine in carbon tetrachloride so as to produce the concentration of titratable iodine (A) shown in the first column.

TABLE I.

$A \times 10^4$.	$[I_2] \times 10^4$.	E.	$[I'] \times 10^4$.	$B \times 10^4$.
0·093	0·078	+0·2331	0·028	+0·028
0·257	0·228	+0·1439	0·020	+0·019
0·743	0·647	+0·1816	0·0077	±
2·16	1·96	+0·2285	0·0022	−0·085

Concentrations are given in mols./litre. E is the $E.M.F.$ measured, referred to the mercurous sulphate electrode. $[I']$ is calculated from the equation $\log [I'] = 1/0{\cdot}05911 \,.\, (E_x - E) + \frac{1}{2} \log [I_2]$. The value of E_x ($= -0{\cdot}0559$ volt) and of the other constants involved are taken from the paper previously mentioned.

It will be seen that B becomes progressively larger as the concentration of iodine diminishes. By comparison with subsequent measurements, this apparent increase is found to be due, not to increased reduction of the iodine, but to the fact that more iodide ions are combined with the starch in concentrated solutions of iodine than in dilute solutions. By extrapolating A to zero, a value of $0{\cdot}035 \times 10^{-4}$ is obtained for B, which is taken to be its true concentration.

Several series of measurements were made with carbon tetrachloride solutions containing different quantities of iodine. The four given on page 1292 are the most consistent of some twelve carried out.

C is the concentration of potassium iodide added, increased by $0{\cdot}35 \times 10^{-5}$, the concentration of iodide ions produced by reduction. D is the concentration of iodide ions combined with the starch, calculated from the equation $D = C + [I^\cdot] - [I'] - [I_3']$. F is the concentration of iodine combined with the starch, calculated from the equation $F = A - [I_2] - [I_3']$.

Two points deserve notice in the above table. The first is the absence of a direct relationship between the iodine taken up by the starch and the concentration either of free iodine (Küster, *Annalen*, 1894, **283**, 360) or of the tri-iodide ion (Lottermoser, *Z. angew. Chem.*, 1924, **37**, 84). This is best seen by comparing the results from different series. The second point is that in dilute iodide solutions the quantity of iodine taken up is approximately double

Table II.

Series I. CCl_4 Sol. = 0·002122*M*.

$A\times10^5$.	$[I_2]\times10^5$.	$E\times10^5$.	$C\times10^5$.	$[I']\times10^6$.	$[I_3']\times10^6$.	$D\times10^5$.	$F\times10^5$.	Log $[I'][I_2]^2$.	Log F.
2·57	2·28	+14·39	0·35	0·199	0·03	0·16	0·29	$\bar{1}5$·015	$\bar{6}$·462
3·02	2·22	+12·53	0·84	0·406	0·06	0·43	0·80	$\bar{1}5$·301	$\bar{6}$·903
4·16	2·08	+10·38	1·94	0·908	0·14	1·02	2·07	$\bar{1}5$·594	$\bar{5}$·316
6·95	1·74	+ 5·45	8·30	5·67	0·71	2·56	5·14	$\bar{1}4$·235	$\bar{5}$·711
12·6	1·05	+ 0·64	40·1	28·6	2·2	11·3	11·3	$\bar{1}4$·499	$\bar{4}$·053
16·5	0·57	− 4·35	199·0	144·0	5·9	54·4	15·3	$\bar{1}4$·670	$\bar{4}$·185

Series II. CCl_4 Sol. = 0·006040*M*.

7·43	6·47	+18·16	0·35	0·077	0·04	0·35	0·96	$\bar{1}5$·508	$\bar{6}$·982
10·34	6·11	+14·63	2·41	0·297	0·13	2·12	4·22	$\bar{1}4$·045	$\bar{5}$·625
15·09	5·53	+12·35	5·49	0·687	0·27	4·78	9·53	$\bar{1}4$·322	$\bar{5}$·979
18·1	5·16	+10·22	10·63	1·52	0·56	9·05	12·9	$\bar{1}4$·607	$\bar{4}$·111
23·0	4·56	+ 7·01	51·8	4·99	1·6	46·7	18·3	$\bar{1}3$·016	$\bar{4}$·262
25·5	4·26	+ 5·91	103·2	7·41	2·3	95·6	21·0	$\bar{1}3$·129	$\bar{4}$·322
30·2	3·68	+ 2·13	157	30·0	8·0	126	25·7	$\bar{1}3$·609	$\bar{4}$·410

Series III. CCl_4 Sol. = 0·01358*M*.

16·2	14·6	+22·56	0·35	0·021	0·02	1·01	1·6	$\bar{1}5$·651	$\bar{5}$·204
18·3	14·3	+21·02	1·38	0·038	0·04	1·71	4·0	$\bar{1}5$·890	$\bar{5}$·602
19·4	14·2	+19·44	2·41	0·070	0·07	2·53	5·2	$\bar{1}4$·149	$\bar{5}$·716
24·6	13·6	+17·84	5·49	0·127	0·12	5·45	11·0	$\bar{1}4$·371	$\bar{4}$·041
30·3	12·9	+13·39	10·63	0·699	0·65	9·88	17·3	$\bar{1}3$·066	$\bar{4}$·238
36·8	12·1	+ 8·44	51·8	4·66	4·0	46·7	24·3	$\bar{1}3$·834	$\bar{4}$·386
40·6	11·6	+ 6·44	103·2	9·95	8·3	92·4	28·2	$\bar{1}2$·127	$\bar{4}$·450

Series IV. CCl_4 Sol. = 0·01819*M*.

21·6	19·6	+22·85	0·35	0·022	0·03	1·20	2·0	$\bar{1}5$·927	$\bar{5}$·301
23·9	19·3	+20·79	1·94	0·048	0·07	2·28	4·6	$\bar{1}4$·252	$\bar{5}$·663
32·3	18·3	+16·71	8·30	0·228	0·30	8·12	14·0	$\bar{1}4$·883	$\bar{4}$·146
40·8	17·2	+ 8·15	19·9	6·23	7·7	12·9	22·8	$\bar{1}2$·265	$\bar{4}$·358
77·1	12·8	− 2·43	415	330	304	55	33·9	$\bar{1}1$·733	$\bar{4}$·530

that of the combined iodide ion. This suggests the formation of a compound of the form StI_5', where St denotes the starch aggregate involved. To examine this point, log*F* (as a measure of the concentration of StI_5') has been plotted against log $[I'][I_2]^2$.

It will be seen that in dilute iodide solutions the points from all four series lie on the same straight line, if allowance be made for experimental error, which must necessarily be large in these very dilute solutions. The equation to the straight line is

$$\log [I'][I_2]^2 = \log F + \bar{1}0{\cdot}42.$$

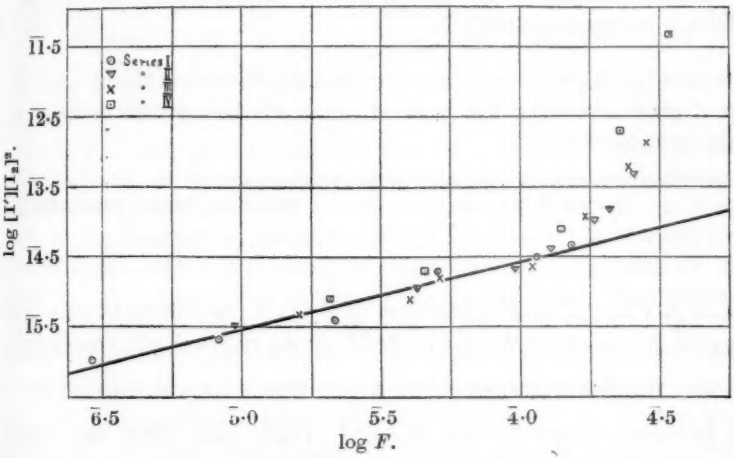
Hence we obtain the somewhat unexpected result,

$$[I'][I_2]^2/F = 2{\cdot}6 \times 10^{-10}.$$

This behaviour is not consistent with the formation of an adsorption compound. It could be explained if an I_5' ion were to dis-

tribute itself between the starch phase and the dispersion medium in a constant ratio. Deviations in the presence of comparatively large concentrations of potassium iodide might be explained by a coagulative effect of the iodide ions. Amongst other reasons, the lack of evidence for the existence of such an ion makes this explanation improbable. A more likely explanation is that an addition compound is formed by the starch with one iodide ion and two iodine molecules. Whilst the starch is in excess, the straight-line relationship found is a close approximation to the truth. In addition, the subsequent shape of the curve is such as we should expect to find. On this hypothesis, the point at which the straight-line relationship ceases to be obeyed corresponds to the point at

FIG. 1.



which the concentration of StI_5' becomes comparable with the original concentration of the starch. We shall not be making an error in orders of magnitude, if we write as an approximation at this point, $[StI_5'] = \frac{1}{10}[St]$ and therefore $[St] = 5F$. Then, writing for the compound formed $(C_6H_{10}O_5)_nI_5'$ and taking $F = 1 \times 10^{-4}$, and the concentration of the starch as 1·25 g./litre, we obtain $n = 15{\cdot}4$. The agreement of this value with the analytical results of Mylius and others is probably due to a certain extent to chance. To obtain complete agreement, it is necessary to assume that the undissociated compound is the hydrogen salt of the above complex anion. The concentration of the hydrogen ions, however, being in considerable excess of those of the other reacting substances, may be considered constant, and does not appear in the mass action relationships.

In dilute iodide solutions, the formation of a compound anion StI_5' is deduced from the equilibrium expression. At higher iodide concentrations, it is obvious from the tabulated results that the iodide ion is taken up in excess of the requirements of this compound, pointing possibly to the formation of StI_3', and even of StI'.

Summary.

The concentrations of the various substances formed when a solution of iodine in carbon tetrachloride is shaken with an aqueous solution of starch, with and without the addition of small quantities of potassium iodide, have been measured and the results tabulated. From considerations based upon these results, it is suggested that an addition compound is formed by the starch, the anion of which, in dilute potassium iodide solutions, has the formula $(C_6H_{10}O_5)_nI_5'$, where n is approximately 15.

I wish to express my thanks to Messrs. Brunner Mond and Co. for a grant covering the cost of some of the apparatus used in this investigation.

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SOUTH KENSINGTON. [*Received, March 24th*, 1925.]

CLXXVI.—*The Formation of* d-2 : 2 : 4-*Trimethyl*cyclo*hexan*-3-*one*-1-*carboxylic Acid from* d-*Camphorquinone.*

By CHARLES STANLEY GIBSON and JOHN LIONEL SIMONSEN.

IT has been shown by one of us (J., 1923, **123**, 2648) that when *d*-longifquinone is heated with an acetic acid solution of hydrogen bromide a keto-acid, $C_{15}H_{24}O_3$, results from the addition of water to the diketone and molecular rearrangement. At the same time, attention was directed to the similarity between this reaction and the action of sulphuric acid on camphorquinone investigated by Manasse and Samuel (*Ber.*, 1897, **30**, 3157; 1902, **35**, 3831) whereby a ketonic acid, $C_{10}H_{16}O_3$, is obtained. In view of the latter reaction having a possible bearing on the former, and consequently on the constitution of *d*-longifolene, we have considered it desirable to investigate the constitution of the keto-acid obtained by Manasse and Samuel, a problem which those authors made little attempt to solve.

Manasse and Samuel did not determine the optical rotatory power of the acid and of its derivatives which we have found to be of considerable service in elucidating the constitution of the

acid. We have confirmed in all respects the previous work, although we have found it much more difficult to obtain the pure acid than the original description led us to expect.

The constitution of the acid was established in the following manner. On oxidation with nitric acid, the keto-acid was converted into a tribasic acid, $C_9H_{14}O_6$, m. p. 156—157°, which, on distillation, was converted into an anhydride, m. p. 98°. Although direct comparison was not possible, there can be little doubt that this acid is β-methylpentane-βγε-tricarboxylic acid (II), which was prepared synthetically by Perkin and Thorpe (J., 1904, **85**, 135). This being the case, the keto-acid, since it is obtained from camphorquinone, may be best represented by formula (I), that is, *d*-2 : 2 : 4-trimethyl*cyclo*hexan-3-one-1-carboxylic acid.*

(I.) $\begin{matrix} CH_2\text{–}CHMe\text{——}CO \\ | \qquad\qquad | \\ CH_2\cdot CH(CO_2H)\cdot CMe_2 \end{matrix}$ $\qquad$ $\begin{matrix} CH_2\cdot CO_2H \\ | \\ CH_2\cdot CH(CO_2H)\cdot CMe_2\cdot CO_2H \end{matrix}$ (II.)

(III.) $\begin{matrix} CH_2\cdot CHMe\text{——}CH\cdot OH \\ | \qquad\qquad | \\ CH_2\cdot CH(CO_2H)\cdot CMe_2 \end{matrix}$ $\qquad$ $\begin{matrix} CH_2\text{—}CMe\text{=}CH \\ | \qquad\quad | \\ CH_2\cdot CH(CO_2H)\cdot CMe_2 \end{matrix}$ (IV.)

It was shown by Manasse and Samuel that when the keto-acid was reduced with sodium amalgam it yielded a hydroxy-acid which showed no tendency to form a lactone; since this acid can only be represented by formula (III) (3-hydroxy-2 : 2 : 4-trimethyl-*cyclo*hexane-1-carboxylic acid) it must be the *trans*-form of the acid. When the *methyl* ester of the hydroxy-acid was treated with phosphorus pentachloride, a mixture of a chloro-ester and unsaturated ester was obtained from which, after treatment with diethylaniline, the pure unsaturated ester was separated. Although the quantity available was insufficient for detailed investigation, there can be little doubt that it was *methyl* 1-2 : 2 : 4-*trimethyl*-Δ^3-cyclo*hexene*-1-*carboxylate* (IV), the acid obtained on hydrolysis being an oil which was lævorotatory in ethyl-alcoholic solution.

Since the keto-acid tended to separate as an oil which crystallised very slowly, we attempted to utilise the crystalline methyl ester for its purification. This ester, in accordance with the statement of Manasse and Samuel, was readily obtained crystalline, but was always obtained mixed with a liquid ester. The mixture distilled as a homogeneous substance, and after the solid had been separated by filtration the liquid portion, possessing the same molecular composition as the solid, could not be induced to crystallise. It therefore appeared possible that this liquid form of the ester con-

* It is conceivable that the hydrolysis may pursue an alternative course which would lead to an acid of the constitution $\begin{matrix} CH_2\cdot CO\text{———}CHMe \\ | \qquad\qquad | \\ CH_2\cdot CH(CO_2H)\cdot CMe_2 \end{matrix}$. This acid and (I) would both give (II) on oxidation.

sisted of an equilibrium mixture of the keto- and enol forms, although it gave no colour with ferric chloride. This view has received support from a careful investigation of the semicarbazones of the ester. The pure crystalline ester on treatment with semicarbazide under suitable conditions (see p. 1300) yielded a mixture of α- and β-semicarbazones. Both these semicarbazones gave on hydrolysis an ester which only partly crystallised, the quantity of crystalline ester obtained from each of them being approximately the same. A mixture of the same two α- and β-semicarbazones was also obtained from the liquid ester and there would therefore appear to be little doubt that the liquid ester is a mixture of the keto- and enol forms. It was, in fact, found possible, starting from 100 grams of the crude acid, to convert all except about 10 grams into the crystalline ester by means of the semicarbazones.

When the pure crystalline methyl ester was hydrolysed with alcoholic potassium hydroxide solution in the usual manner, the acid obtained on acidification still tended to separate as an oil and, although eventually crystallising as a hard cake, it had not the appearance of a homogeneous substance. A quantity of the acid was therefore crystallised from water and separated into two main fractions which melted respectively at 71—72° and 65—69°. When examined polarimetrically in alcoholic solution, the two fractions showed a marked difference in rotatory power, the specific rotation of the first fraction being very much higher than that of the second. When dissolved in sodium hydroxide, the specific rotation of the first fraction was again higher than that of the second fraction and mutarotation from a higher to a lower value was also observed, the relative change in rotatory power being practically the same in both cases. These observations explained at once the great difficulty experienced in purifying the acid even when prepared from the pure ester, since it was clear that the acid undergoes racemisation in alkaline solution. This is accounted for by the fact that a change from the enol to the keto-form involves one of the asymmetric carbon atoms and although in this reversible change complete racemisation is unlikely owing to the presence of the second asymmetric carbon atom in the molecule, yet partial racemisation is sure to take place.*

* Another explanation of the above phenomena which may not involve a keto $\rightleftharpoons$ enol change in the case of γ- or δ-keto-acids and esters is the following: the keto-acid and ester possess two centres of asymmetry, $-CH_2-{}^*CHMe-CO-$ and $-CH_2-{}^*CH(CO_2H)-CMe_2-$, which may be distinguished as *X* and *Y* respectively. *X* may easily suffer racemisation and *Y* would be more difficult to racemise. On this view, the crystalline ester would be "$+X+Y$" and the liquid ester an equilibrium mixture "$+X+Y-X+Y$."

Reference has been made above to the fact that the methyl ester gave rise to two semicarbazones. When the preparation was carried out using sodium acetate to liberate the semicarbazide, the yield of the β-semicarbazone was very small, whilst if sodium bicarbonate or potassium carbonate was used the β-form was the main product of the reaction. This indicated that the β-form is unstable and tends to pass into the α-form in the presence of acetic acid. This has been confirmed by polarimetric observations. A solution of the α-form in acetic acid showed a small but definite mutarotation from a higher to a constant lower value; a mixture of the α- and β-forms showed a much more marked mutarotation, whilst the α-form showed a considerable mutarotation from a lower to a constant higher value, the final value being the same in all three cases.

That the mutarotation was due to the acetic acid was proved by the fact that the β-semicarbazone showed no mutarotation when dissolved in alcohol (owing to its sparing solubility the α-semicarbazone could not be examined in this solvent), but on the addition of a small quantity of acetic acid mutarotation was observed. The semicarbazones have optical rotatory powers of opposite sign to those of the corresponding acid and methyl ester.

A somewhat analogous case of the conversion of a *syn*- into an *anti*-form (or *vice versa*) accompanied by mutarotation was observed by Forster (J., 1905, **87**, 237), who showed that of the three oximes formed from *iso*nitrosocamphor on treatment with magnesium methyl iodide, the α-oxime passed into the γ-oxime when exposed to light in chloroform solution, the change being accompanied by a diminution in the specific rotation. By removal of the solvent Forster recovered the whole of the α-oxime in the form of the γ-oxime. In the case of the semicarbazones, we have not been equally successful owing to the difficulty of removing the acetic acid, but we have established the fact that from all the solutions only the stable α-form could be separated. In our opinion there can be no doubt that the mutarotation is caused by the change of the unstable β-form to the stable α-form, the final observed rotation being that of the equilibrium mixture of the two. Apart from the above, it should be noted that the rotatory power of the pure α-semicarbazone in acetic acid solution falls from a higher to a lower value; that of the pure β-semicarbazone rises from a low value to a higher value and then falls again to the constant value, higher than that observed at first; whilst mixtures of the two show rotatory powers which at the beginning are higher than any recorded in the cases of the pure semicarbazones and which fall to the lower constant values. It would appear that this case of

mutarotation is worthy of detailed investigation. Tentatively, we suggest that the results obtained point to the formation of an intermediate compound (? salt formation) of high rotatory power in the conversion of the β- into the α-form and that this has not been observed in the conversion of the α- into the β-form.

It is hoped by extending this work to the investigation of substituted camphorquinones to throw some light on the question of the constitution of the β-derivatives of camphor.

EXPERIMENTAL.

d-2 : 2 : 4-*Trimethyl*cyclo*hexan*-3-*one*-1-*carboxylic acid* (I), prepared by Manasse and Samuel's method (*loc. cit.*), was obtained as an oil which only partly crystallised. It was purified most conveniently by conversion into the methyl ester by treatment with methyl alcohol and sulphuric acid, when, on extraction with ether and removal of the solvent, the ester was obtained as an oil which rapidly partly crystallised in long needles. The solid ester was separated and the oil, which as a rule formed 60% of the total yield, was reserved for later investigation (see below).

Methyl *d*-2 : 2 : 4-trimethyl*cyclo*hexan-3-one-1-carboxylate crystallised from dilute methyl alcohol in fine, long needles which melted, as stated by Manasse and Samuel, at 82—83°. The ester was readily volatile in steam, and sublimed in a vacuum at the ordinary temperature (Found: C, 66·6; H, 9·0. Calc., C, 66·6; H, 9·1%).

The rotatory power was determined at 15° in ethyl-alcoholic solution; $c = 0{\cdot}9908$, $l = 4$, $\alpha_{5461} = +2{\cdot}55°$, $[\alpha]_{5461} = +64{\cdot}33°$.

After hydrolysis of the ester with alcoholic potassium hydroxide solution, the acid separated on acidification of the aqueous alkaline solution as a viscid oil which slowly crystallised when kept at 0°. The acid crystallised from water in needles, m. p. 71—72°. On allowing the mother-liquor to evaporate slowly in a vacuum desiccator over sulphuric acid, crystals and some oil slowly separated. The material was collected and again crystallised from water with the same result. The crystalline solid melted at 67—69°, softening somewhat at 60°. As has already been mentioned, the explanation of this apparent non-homogeneity of the acid prepared from the pure crystalline ester was explained by partial racemisation accompanied by enol-keto change.

In ethyl-alcoholic solution at 15°, the acid shows no mutarotation: first fraction, $c = 1{\cdot}0346$, $l = 4$, $\alpha_{5461} = +1{\cdot}96°$, $[\alpha]_{5461} = +47{\cdot}4°$; second fraction, $c = 0{\cdot}9626$, $l = 4$, $\alpha_{5461} = +0{\cdot}72°$, $[\alpha]_{5461} = +18{\cdot}7°$.

A solution of the acid in a very slight excess of the calculated

quantity of aqueous sodium hydroxide displayed definite mutarotation at 15°; the rotatory power was constant after 48 hours: first fraction, $c = 0{\cdot}9784$, $l = 4$, $\alpha_{5461} = +0{\cdot}87°$, $[\alpha]_{5461} = +22{\cdot}2°$, changing to the constant values $\alpha_{5461} = +0{\cdot}59°$ and $[\alpha]_{5461} = +15{\cdot}1°$; second fraction, $c = 1{\cdot}0226$, $l = 4$, $\alpha_{5461} = +0{\cdot}33°$, $[\alpha]_{5461} = +8{\cdot}1°$, the final values being $\alpha_{5461} = +0{\cdot}21°$ and $[\alpha]_{5461} = +5{\cdot}1°$.

The semicarbazone, prepared in the usual manner, was obtained as a very sparingly soluble crystalline powder which, after crystallisation from a large volume of alcohol, decomposed at 228—229°, a somewhat higher melting point than that observed by Manasse and Samuel (Found: C, 54·9; H, 7·7. Calc., C, 54·8; H, 7·9%).

The α-oxime, prepared in alkaline solution as described by Manasse and Samuel, melted at 164—165°; if, however, the oxime was prepared in alcoholic solution, sodium acetate being used to decompose the hydroxylamine hydrochloride, a β-*oxime* was obtained which differed from the α-oxime in being much more sparingly soluble in alcohol, from which it crystallised in thin plates decomposing at 226° (Found: N, 7·2. $C_{10}H_{17}O_3N$ requires N, 7·0%).

The filtrate from which the crystalline ester had been separated was distilled under diminished pressure, when practically the whole distilled as a colourless, viscid oil at 146—155°/20 mm. On keeping in the ice-chest for some days, the oil partly solidified; the crystals, which consisted of the ester, m. p. 83°, were collected and the oil was redistilled, when it boiled at 135—140°/10 mm. Analysis showed this to be the pure methyl ester and, as has been suggested above, it was in all probability an equilibrium mixture of the keto- and enol forms. In alcoholic solution, it gave no colour with ferric chloride (Found: C, 66·2; H, 9·4. $C_{11}H_{18}O_3$ requires C, 66·6; H, 9·1%).

The *oxime*, prepared by treating either the crystalline or the liquid ester with hydroxylamine hydrochloride in alcoholic solution in the presence of sodium acetate, was obtained on removal of the solvent as a semi-solid oil and evidently consisted of a mixture of the *syn*- and *anti*-forms. The crude oxime was drained on porous porcelain until free from adhering oil and crystallised from dilute methyl alcohol, from which it was obtained in colourless needles, m. p. 110—111° (Found: C, 62·0; H, 9·1. $C_{11}H_{19}O_3N$ requires C, 62·0; H, 8·9%).

The oxime did not undergo the Beckmann rearrangement when treated with pyridine and benzenesulphonyl chloride and was recovered unchanged after treatment with these reagents.

The α- and β-Semicarbazones of Methyl d-2 : 2 : 4-*Trimethylcyclohexan*-3-*one*-1-*carboxylate.*

(i) The *α-semicarbazone* was most readily prepared in a pure state on treatment of the methyl ester (either solid or liquid) in alcoholic solution with an aqueous solution of semicarbazide acetate. The *semicarbazone*, which separated as a thick, white precipitate (yield about 70%), crystallised from much alcohol in glistening leaflets which sintered at 229—230° and decomposed at 231° (Found: C, 56·4; H, 8·1. $C_{12}H_{21}O_3N_3$ requires C, 56·5; H, 8·2%).

The optical rotatory power was determined at 15° in acetic acid solution, definite, but small, mutarotation being observed: $c = 0{\cdot}9540$, $l = 4$, $\alpha_{5461} = -2{\cdot}13°$, $[\alpha]_{5461} = -55{\cdot}8°$; the final values, after 48 hours, being $\alpha_{5461} = -1{\cdot}91°$, $[\alpha]_{5461} = -50{\cdot}5°$.

When the mother-liquor of the α-semicarbazone was diluted with water and allowed to remain for several days in the ice-chest, a small quantity of the impure β-semicarbazone, fine needles, m. p. about 150°, was deposited.

(ii) *β-Semicarbazone.*—The methyl ester dissolved in alcohol was mixed with a slight excess of an aqueous solution of semicarbazide hydrochloride to which sufficient sodium bicarbonate had been added to neutralize the hydrochloric acid. On standing for some days with occasional agitation, the semicarbazone separated as a white, crystalline precipitate, which was washed with a little ether and dried on porous porcelain (yield 11 g. from 10 g. of ester). This crude semicarbazone, m. p. about 180°, the rotation of which could not be determined accurately, was dissolved in the minimum of hot alcohol and allowed to crystallise, when colourless leaflets were obtained which softened at 210° and decomposed at 215—216° (A) (yield 3·1g.) (Found: C, 56·8; H, 8·3%).

In acetic acid solution at 15°, mutarotation in the same direction from a high value to the same constant value, reached after 48 hours, was observed: $c = 1{\cdot}0140$, $l = 4$, $\alpha_{5461} = -2{\cdot}89°$, $[\alpha]_{5461} = -71{\cdot}25°$; the final values being $\alpha_{5461} = -2{\cdot}05°$, $[\alpha]_{5461} = -50{\cdot}5°$.

Fraction (A), recrystallised from alcohol, gave nearly pure α-semicarbazone, decomp. 221—222°. The optical activity was observed under the same conditions as before, but the constant value was not reached after 40 hours: $c = 1{\cdot}0686$, $l = 4$, $\alpha_{5461} = -2{\cdot}90°$, $[\alpha]_{5461} = -67{\cdot}8°$: after 40 hours the values observed were $\alpha_{5461} = -2{\cdot}23°$, $[\alpha]_{5461} = -52{\cdot}2°$.

The original mother-liquor from which fraction (A) had been separated was concentrated to a small bulk under diminished

pressure,* when, on cooling, a large fraction crystallised in soft needles which softened at 158° and melted at 161°. The β-*semicarbazone*, which was very readily soluble in alcohol, crystallised from dilute methyl alcohol in fine needles, m. p. 161—162° (Found : C, 56·4; H, 7·9%). In acetic acid solution at 15°, the β-semicarbazone shows a mutarotation which rises and falls again to the same constant value, after about 60 hours, as was observed in the other cases. The various observed rotations are quoted : $c = 1{\cdot}0464$, $l = 4$, $\alpha_{5461} = -1{\cdot}60°, -1{\cdot}78°, -2{\cdot}24°, -2{\cdot}19°, -2{\cdot}10°$; $[\alpha]_{5461} = -38{\cdot}2°, -42{\cdot}5°, -53{\cdot}5°, -52{\cdot}3°, -50{\cdot}2°$.

In ethyl alcohol at the same temperature, no mutarotation was observed during 24 hours : $c = 0{\cdot}9896$, $l = 4$, $\alpha_{5461} = -0{\cdot}73°$.

When the solution (volume 49·25 c.c.) was poured out of the tube and mixed thoroughly with acetic acid (0·75 c.c.), marked mutarotation was observed, the following being the various rotations noted during 72 hours : $-0{\cdot}80°$, $-0{\cdot}85°$, $-0{\cdot}99°$, $-1{\cdot}13°$, $-1{\cdot}26°$.

Hydrolysis of the α- and β-Semicarbazones.—Both the α- and the β-semicarbazone yielded a mixture of a crystalline and a solid methyl ester on hydrolysis.

(i) The α-semicarbazone (9 g.) was heated on the water-bath with sulphuric acid (5% ; 25 c.c.) until a clear solution was obtained, the ester was taken up with ether, the ethereal extract washed with sodium carbonate solution, dried, and the solvent removed, when a semi-crystalline oil (7 g.) remained which on filtration yielded 4·6 g. of the crystalline ester.

(ii) The β-semicarbazone (6·8 g.), when hydrolysed under similar conditions, yielded the mixed ester (5 g.), from which 2·1 g. of crystalline ester were separated.

Oxidation of d-2 : 2 : 4-*Trimethylcyclohexan-3-one-1-carboxylic Acid with Nitric Acid.* β-*Methylpentane-βγε-tricarboxylic Acid* (II).

A mixture of the keto-acid (10 g.) with nitric acid (*d* 1·27; 250 c.c.) was heated on the water-bath for 3 hours and finally on the sand-bath for 3 hours to complete the reaction. The excess of mineral acid was removed under diminished pressure and finally in a vacuum desiccator over sodium hydroxide, when a viscid oil remained which slowly crystallised. It was best purified by conversion into the triethyl ester, which distilled almost completely at 185—190°/20 mm. The pure ester was hydrolysed with hydrochloric acid, and the crystalline residue which remained after the

* Owing to the distinct volatility of the β-semicarbazone, loss of material could not be avoided during its preparation.

removal of the excess of mineral acid was recrystallised from hydrochloric acid. It melted at 155—157° with loss of water, the m. p. being dependent on the rate of heating. The identity of the acid with that prepared synthetically by Perkin and Thorpe (*loc. cit.*) was confirmed by analysis (Found: C, 69·4; H, 6·3; *M*, 218·4. Calc., C, 69·5; H, 6·4%; *M*, 218) and by conversion, on distillation under diminished pressure, into the anhydride, a viscid oil which gradually crystallised in stellate groups of needles and separated from benzene in plates, m. p. 98° * (Found: C, 53·9; H, 5·9. Calc., C, 54·0; H, 6·0%).

trans-d-3-*Hydroxy*-2 : 2 : 4-*trimethyl*cyclo*hexane*-1-*carboxylic Acid* (III) *and* 1-2 : 2 : 4-*Trimethyl*-Δ^3-cyclo*hexene*-1-*carboxylic Acid* (IV).

The *trans*-hydroxy-acid was readily obtained from the keto-acid by Manasse and Samuel's method (*loc. cit.*). In solution in ethyl alcohol at 15°, it was of the same sign as the keto-acid; no mutarotation was observed: $c = 1{\cdot}0146$, $l = 4$, $\alpha_{5461} = +1{\cdot}77°$, $[\alpha]_{5461} = +43{\cdot}6°$.

The *methyl* ester was a somewhat viscid, colourless oil, b. p. 150—152°/12 mm. (Found: C, 66·2; H, 9·4. $C_{11}H_{20}O_3$ requires C, 66·0; H, 10·0%).

For the preparation of the unsaturated ester, a solution of the hydroxy-ester (18 g.) in ether (100 c.c.) was cooled with ice and gradually treated with finely-divided phosphorus pentachloride (20 g.), which dissolved readily; the reaction was completed by gentle warming. After the addition of ice the ethereal solution was thoroughly washed with sodium carbonate solution (A), dried, and evaporated. The residual oil was distilled, when the bulk of the oil passed over at 120—140°/20 mm. The mixture of chloro- and unsaturated esters was boiled with an excess of diethylaniline for some hours. The ester, which was separated in the usual manner, was fractionated under diminished pressure, when a large fraction was obtained, b. p. 105—107°/14 mm. (Found: C, 72·4; H, 9·8. $C_{11}H_{18}O_2$ requires C, 72·4; H, 10·0%).

Methyl 1-2 : 2 : 4-*trimethyl*-Δ^3-cyclo*hexene*-1-*carboxylate*, a colourless, fragrant-smelling oil, gave, when hydrolysed with alcoholic potassium hydroxide solution in the usual manner, the *acid* as a very viscid oil, b. p. 150—152°/16 mm. (Found: C, 70·7; H, 8·7. $C_{10}H_{16}O_2$ requires C, 71·4; H, 9·6%). The acid did not give any indication of mutarotation in ethyl-alcoholic solution during

* In Richter's "Lexikon," Vol. I., p. 1134, the m. p. of the anhydride is wrongly given as 155—157°, which is the m. p. of the acid. The b. p. is also wrongly stated to be 255° instead of 255°/45 mm.

24 hours. Its optical rotatory power is opposite to that of the keto- and of the hydroxy-acid: $c = 2{\cdot}653$, $l = 4$, $\alpha_{5461} = -4{\cdot}08°$, $[\alpha]_{5461} = -38{\cdot}5°$.

1-2 : 2 : 4-*Trimethyl*-Δ^3-cyclo*hexene*-1-*carboxylic acid* could not be induced to crystallise even when kept for several weeks in the ice-chest; in sodium carbonate solution it immediately decolorised a solution of potassium permanganate, whilst in chloroform solution bromine was rapidly absorbed, but the bromo-acid formed decomposed with evolution of hydrogen bromide. The *ammonium* salt, which was somewhat sparingly soluble in water, crystallised in irregular plates, decomp. 147—148°. The *calcium*, *barium*, and *silver* salts were all sparingly soluble in water; the silver salt was analysed (Found: Ag, 39·3. $C_{10}H_{15}O_2Ag$ requires Ag, 39·3%).

The sodium carbonate solution (A) (see above) was acidified, when a viscid oil separated; this was taken up with ether, the ether dried, and evaporated. The residual oil (5 g.) was triturated with dilute ammonia, when a small quantity of an insoluble oil remained which partially crystallised. The solid was collected, drained on porous porcelain, and recrystallised from dilute methyl alcohol. It was identified as methyl *d*-2 : 2 : 4-trimethyl*cyclo*hexan-3-one-1-carboxylate, m. p. 82—83°, mixed m. p. 82—83° (Found: C, 67·0; H, 9·1. Calc., C, 66·6; H, 9·1%). The separation of the keto-ester from a sodium carbonate solution is somewhat remarkable, since experiment has shown the crystalline ester to be quite insoluble in cold alkali. It is possible that it dissolved in its enolic form, and this point will be further investigated.* The oil which dissolved in the ammonia was found to consist of the *cyclo*hexene acid.

In conclusion, the authors wish to express their thanks to the Government Grant Committee of the Royal Society for a grant which has defrayed part of the expense of this investigation, and to Mr. F. B. Windle for his assistance in the analytical work.

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* It is very improbable that the presence of the keto-ester in the sodium carbonate solution was due to any defect in manipulation, since the same result was obtained in two distinct experiments.

CLXXVII.—*The Action of Halogens on Phenylhydrazones. Part II. The Action of Chlorine.*

By JAMES ERNEST HUMPHRIES, HENRY HUMBLE, and ROY EVANS.

THE action of chlorine on phenylhydrazones in cold carbon tetrachloride solution differs from that of bromine (Humphries, Bloom, and Evans, J., 1923, 123, 1766) in that, whilst bromine enters the benzene nucleus atom by atom, first in the para-position and then in the ortho-position to the group RR′C:N·NH·, chlorination leads directly to the 2 : 4-dichloro-derivative RR′C:N·NH·$C_6H_3Cl_2$, even when the phenylhydrazone is present in large excess. Moreover, bromination ceases when the dibromophenylhydrazone has been formed, but chlorination proceeds, although with difficulty, a stage farther with formation of the 2 : 4 : 6-trichlorophenylhydrazone.

Benzaldehydephenylhydrazone is converted by the action of an excess of chlorine into a *tetrachloro*-derivative,

$$C_6H_5\cdot CCl{:}N\cdot NH\cdot C_6H_2Cl_3,$$

which is also formed, quantitatively, by the interaction of chlorine (1 mol.) and benzaldehyde-2 : 4 : 6-trichlorophenylhydrazone. This type of substitution occurs, as in the case of the bromination of benzaldehydephenylhydrazone, after chlorine has entered the ortho- and para-positions, the compound $C_6H_5\cdot CCl{:}N\cdot NH\cdot C_6H_3Cl_2$ (2 : 4) being formed readily from the phenylhydrazone, *p*-chlorophenylhydrazone, and 2 : 4-dichlorophenylhydrazone of benzaldehyde. The trichloro-compound cannot be converted into the tetrachloro-compound by the action of chlorine alone. The presence of hydrogen chloride is necessary to produce the change; for example, the conversion is readily effected at 0° in the presence of phenol.

The primary product of chlorination of a phenylhydrazone is a yellow or orange, usually unstable, precipitate similar to those obtained in the bromination experiments; it consists of the hydrochloride of the chlorophenylhydrazone or of a mixture of the hydrochlorides of the chlorophenylhydrazone and the original phenylhydrazone, according to the proportion of chlorine employed in the experiment.

The stability of a hydrazone towards hydrolysis by an acid depends not only on the nature of the aldehydic or ketonic constituent (*loc. cit.*, p. 1767), but also on the strength of the basic one, in which respect phenylhydrazine < *p*-bromophenylhydrazine < 2 : 4-dibromophenylhydrazine, for when, *e.g.*, benzaldehyde-*p*-bromophenylhydrazone is brominated the final product contains *p*-bromophenylhydrazine hydrobromide and benzaldehyde-2 : 4-dibromophenylhydrazone. A corresponding relationship in the case

of the Schiff's bases is evident from the work of Franzen and Henglein (*J. pr. Chem.*, 1915, **91**, 245), for whilst the dibromides of benzylideneaniline and benzylidene-*p*-bromoaniline gave the hydrobromides of benzylidene-*p*-bromoaniline and benzylidene-2 : 4-dibromoaniline respectively on boiling with alcohol, the dibromide of benzylidene-2 : 4-dibromoaniline decomposed immediately under the same treatment, yielding only 2 : 4 : 6-tribromoaniline. Here again the stability varies with the strength of the basic constituent, in which respect aniline > *p*-bromoaniline > 2 : 4-dibromoaniline.

EXPERIMENTAL.

Preparation of the Chlorophenylhydrazines.—Reduction with stannous chloride of the diazonium salts obtained from *p*-chloro-, 2 : 4-dichloro-, and 2 : 4 : 6-trichloro-aniline having given very poor yields of the corresponding hydrazines, Davies's method (reduction with ammonium sulphite; J., 1922, **121**, 719) was employed. Since little or no ammonium phenylhydrazinedisulphonate separated from the reaction mixture, this was heated at 80° with concentrated hydrochloric acid, when the hydrochloride of the base separated. *p*-Chloro- and 2 : 4-dichloro-phenylhydrazine were thus obtained in yields of 95%. The yield of 2 : 4 : 6-trichlorophenylhydrazine was only 25%, owing to the simultaneous formation of a brown oil, which solidified on cooling and from which white needles, m. p. 64°, of 1 : 3 : 5-trichlorobenzene were obtained in considerable quantity (Found : Cl, 58·9. Calc., Cl, 58·7%).

Chlorination of Phenylhydrazones.

Chlorination was effected by mixing well-cooled solutions (−5° to −10°) of chlorine (1 mol., unless stated otherwise) and the phenylhydrazone (1 mol.) in carbon tetrachloride. Usually the temperature rose slightly and an unstable, tarry precipitate formed. This, the primary product, was dissolved in alcohol; the final products were obtained from the alcoholic solution.

The identity of the final products was established by analysis and, in the case of phenylhydrazones, by comparison with synthetically prepared specimens, or in the case of phenylhydrazines, by condensation with benzophenone or benzaldehyde and comparison of the product with the corresponding phenylhydrazone.

Acetonephenylhydrazone.—The pale yellow, crystalline, primary product, which became almost colourless when washed with ether, was dried in a vacuum [Found : Cl (as hydrochloride), 16·4; Cl (total), 32·9%]. These results are very close to those required for the hydrochloride of acetonemonochlorophenylhydrazone (16·2 and 32·4 respectively). Addition of ether to the cold alcoholic

solution of the primary product gave a precipitate only if the alcoholic solution had been previously boiled. This precipitate was probably a mixture of the hydrochlorides of phenylhydrazine and 2 : 4-dichlorophenylhydrazine, for a determination of the equivalent weight of the base in it gave the value required for monochlorophenylhydrazine, and combination with benzophenone produced a mixture from which a considerable quantity of benzophenonephenylhydrazone was obtained (no other pure hydrazone was isolated).

Acetophenonephenylhydrazone.—A solution in cold alcohol of the yellow primary product deposited crystals of phenylhydrazine hydrochloride, and from the mother-liquor were obtained yellow needles, m. p. 85°, of *acetophenone-2 : 4-dichlorophenylhydrazone* (Found : Cl, 25·95. $C_{14}H_{12}N_2Cl_2$ requires Cl, 25·45%).

Benzophenonephenylhydrazone.—From the yellow alcoholic solution of the primary product (even if excess of hydrazone had been used) was obtained a mixture of the original phenylhydrazone and pale-yellow needles (m. p. 105°) of *benzophenone-2 : 4-dichlorophenylhydrazone* (Found : Cl, 20·3. $C_{19}H_{14}N_2Cl_2$ requires Cl, 20·8%).

Benzophenone-2 : 4-dichlorophenylhydrazone.—No substitution took place at 0°. If the hydrazone and halogen were left in contact for 24 hours at the laboratory temperature about one-half of the hydrazone was converted into the *2 : 4 : 6-trichlorophenylhydrazone*, m. p. 106° (Found : Cl, 28·3. $C_{19}H_{13}N_2Cl_3$ requires Cl, 28·4%).

Benzaldehydephenylhydrazone.—The final product of chlorination with 1 mol. of chlorine was a mixture of benzaldehydechlorophenylhydrazones which could not be separated from one another; with 3 mols. of chlorine, the compound $C_6H_5\cdot CCl{:}N\cdot NH\cdot C_6H_3Cl_2$ (2 : 4) was obtained; and with excess of chlorine, a tetrachloro-derivative, $C_6H_5\cdot CCl{:}N\cdot NH\cdot C_6H_2Cl_3$ (2 : 4 : 6).

Benzaldehyde-p-chlorophenylhydrazone.—The final product was a mixture of the original phenylhydrazone and the compound $C_6H_5\cdot CCl{:}N\cdot NH\cdot C_6H_3Cl_2$ (2 : 4), m. p. 90° (Found : Cl, 35·6. $C_{13}H_9N_2Cl_3$ requires Cl, 35·6%).

Benzaldehyde-2 : 4-dichlorophenylhydrazone.—The yellow primary product, while still in suspension in carbon tetrachloride, was treated with a little alcohol, part of the former solvent was removed by distillation, and more alcohol added, when the preceding trichloro-compound rapidly crystallised in needles (yield quantitative). Its properties are very similar to those of the corresponding bromine compound (*loc. cit.*, p. 1771). Reduction in boiling alcoholic solution with zinc dust (6 hours), followed by concentration of the solution and addition of ether and hydrogen chloride, gave 2 : 4-dichlorophenylhydrazine hydrochloride in good yield, and from

this hydrazine were prepared m-*chlorobenzaldehyde*-2 : 4-*dichlorophenylhydrazone*, yellow prisms, m. p. 127° (Found : Cl, 35·6. $C_{13}H_9N_2Cl_3$ requires Cl, 35·6%), and p-*chlorobenzaldehyde*-2 : 4-*dichlorophenylhydrazone*, white needles, m. p. 117° (Found : Cl, 35·7%). The properties of these hydrazones confirm the above formula of the trichloro-compound (compare note below).

Benzaldehyde-2 : 4 : 6-*trichlorophenylhydrazone*.—This experiment, carried out like the preceding one, gave the *tetrachloro*-compound, $C_6H_5{\cdot}CCl{:}N{\cdot}NH{\cdot}C_6H_2Cl_3$ (2 : 4 : 6), yellow needles, m. p. 98°, in quantitative yield (Found : C, 46·3; H, 2·4; Cl, 42·3; *M*, in freezing benzene, 347. $C_{13}H_8N_2Cl_4$ requires C, 46·7; H, 2·4; Cl, 42·5%; *M*, 344).

The product was reduced with zinc dust in boiling alcohol (1—2 hours), and 2 : 4 : 6-trichlorophenylhydrazine hydrochloride ultimately obtained (Found : Cl, 57·6; equiv., 213.

$$C_6H_2Cl_3{\cdot}NH{\cdot}NH_2,HCl$$

requires Cl, 57·25%; equiv., 211·5). This is probably the best method of preparing 2 : 4 : 6-trichlorophenylhydrazine.

Benzaldehydephenylhydrazone is not reduced by zinc dust in alcoholic solution as are the above chloro-derivatives, which have the hydrogen of the original aldehyde group replaced by halogen.

NOTE.—The compound (white, silky needles, m. p. 114°) to which Humphries, Bloom, and Evans (*loc. cit.*, p. 1771) assigned the formula $C_6H_5{\cdot}CBr{:}N{\cdot}NH{\cdot}C_6H_3Br_2$ was stated by Ciusa and Vecchiotti (*Gazzetta*, 1916, **46**, i, 240) to be *p*-bromobenzaldehyde-2 : 4-dibromophenylhydrazone. We have prepared the latter compound; it is orange-yellow and melts at 128° (Found : Br, 55·2. $C_{13}H_9N_2Br_3$ requires Br, 55·4%).

One of us (H. H.) is indebted to the Robbie Fund for a Research Scholarship. We desire to express our thanks for a grant from the Chemical Society.

UNIVERSITY OF ABERDEEN. [*Received, February 4th*, 1925.]

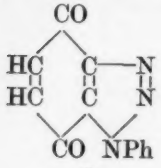
CLXXVIII.—*The Action of Azides on Toluquinone.*

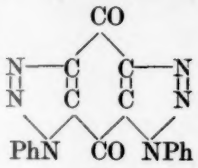
By FREDERICK DANIEL CHATTAWAY and GEORGE DAVID PARKES.

THE action of azides on quinones was first studied by Wolff and various collaborators (*Annalen*, 1912, **394**, 70; 1913, **399**, 274).

From phenyl azide and benzoquinone Wolff obtained four products besides quinhydrone, *viz.*, a triazole, phenylazimino-

quinone (I); two bisaziminoquinones (II and III); and a compound, which formed the bulk of the product, of the composition


(I.)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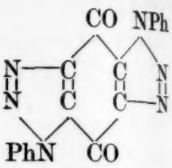
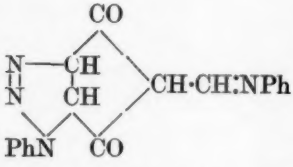
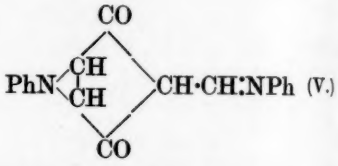

(III.)

$C_{18}H_{14}O_2N_4$, for which he later suggested the constitution (IV) from analogy with the constitution he assigned to a corresponding derivative obtained from naphthaquinone. He found that this compound on heating lost nitrogen and yielded a compound of the composition $C_{18}H_{14}O_2N_2$ which he assumed to have the constitution (V).

(IV.) 

 (V.)

The first condensation product would be expected to contain two hydrogen atoms more than Wolff's compound (I). These, however, he suggested had been oxidised off by the excess of quinone used, thereby accounting for the presence of quinhydrone in the product of the reaction.

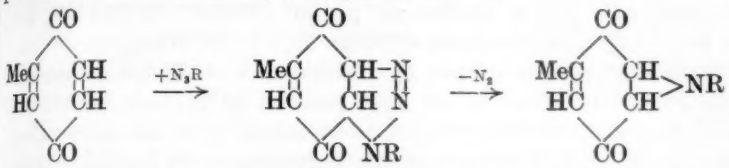
Somewhat similar results were obtained with α-naphthaquinone, but the initial triazole could not be isolated in a pure state.

The work described in the present paper was undertaken with the idea that the condensation would probably follow a simpler course with toluquinone, and that some of the doubtful points in Wolff's conclusions might be put to the test.

The action of azides on toluquinone yields first the anticipated triazoles; the azide reacting with only one double bond (and therefore probably not that contiguous to the methyl group) in the toluquinone molecule.

These triazoles are very unstable and cannot as a rule be isolated in a pure state, but pass with loss of nitrogen into compounds of the composition $R{\cdot}C_7H_6O_2N$. There seems no reason to suppose that when loss of nitrogen occurs the six-carbon atom ring of the toluquinone nucleus becomes a five-atom ring, or that in the original product two hydrogen atoms have been removed by oxidation, since no trace of quinhydrone could be detected in the reaction products. It seems more likely that these substances should be

represented as containing rings of six and three atoms, respectively, having two carbon atoms in common. The formation and decomposition of the triazole may be represented thus :



A series of these compounds has been prepared. The one obtained by the condensation of *o*-tolyl azide with toluquinone was found to be the most convenient for investigating the properties of the final product.

EXPERIMENTAL.

Preparation of Toluquinone.—Toluquinone is easily made by the oxidation of *o*-toluidine by means of potassium dichromate, or manganese dioxide, and sulphuric acid (compare *Ber.*, 1887, **20**, 2283). The chief difficulty in the process is the isolation of the quinone from the reaction product. The following procedure has been found to yield the most satisfactory results.

A solution of 30 g. of *o*-toluidine in a mixture of 240 g. of concentrated sulphuric acid and 900 c.c. of water is well cooled in a freezing mixture, and stirred vigorously while 78 g. of finely powdered potassium dichromate are added slowly in portions of about 1 g. at a time. The stirring is continued for about ½ hour after all the dichromate has been added, and the mixture is kept for 12 hours. The toluquinone which separates is filtered off and distilled *in small portions at a time* in a current of superheated steam. The quinone suffers some decomposition when distilled, but this is reduced to a minimum by the method described, as the amount of decomposition appears to depend on the duration of the operation.

The azides required were prepared from the corresponding diazonium tetrachloroiodides as described by Chattaway, Garton, and Parkes (J., 1924, **125**, 1980).

Action of Phenyl Azide on Toluquinone and Formation of Phenylcycloiminotoluquinone.—A solution of 10 g. of toluquinone and 10 g. of phenyl azide in 30 c.c. of dry benzene was maintained at 50° for 20 hours. The dark brown solid that separated on cooling was washed with a little benzene, then repeatedly with ether to remove any unchanged toluquinone, and the buff-coloured residue of *phenylaziminotoluquinone* was recrystallised from warm acetone, in which it was fairly soluble, separating in small, yellow plates, m. p. 206° (darkening at about 190°) (Found : C, 64·9; H, 4·5; N, 17·4. $C_{13}H_{11}O_2N_3$ requires C, 64·7; H, 4·6; N, 17·4%).

On prolonged heating with benzene or on heating for a few minutes with aniline this compound loses nitrogen and passes into *phenyl*cyclo*iminotoluquinone*, which separates from boiling benzene in small, pale yellow needles, m. p. 130° (Found: C, 73·4; H, 5·2; N, 6·5. $C_{13}H_{11}O_2N$ requires C, 73·2; H, 5·1; N, 6·6%).

Action of o-Tolyl Azide on Toluquinone.—*o*-Tolylaziminotoluquinone, which must be the first product of the condensation of *o*-tolyl azide and toluquinone, is obtained as a microcrystalline powder, m. p. 155°, when equivalent quantities are heated together in chloroform solution. It cannot, however, be obtained perfectly pure, as it evolves nitrogen during recrystallisation.

If benzene be used instead of chloroform, owing to its higher boiling point, complete loss of nitrogen occurs during the heating and *o*-tolyl*cyclo*iminotoluquinone only is obtained.

Formation of o-*Tolyl*cyclo*iminotoluquinone.*—A solution of 20 g. of toluquinone (2 mols.) and 15 g. of *o*-tolyl azide (1 mol.) in 80 c.c. of benzene was heated under reflux for 10 hours. The benzene was then evaporated off and ether added to the dark brown, pasty residue, when *o*-tolyl*cyclo*iminotoluquinone separated as a yellow, microcrystalline powder, which was thoroughly washed with ether to remove any unchanged toluquinone. It was recrystallised several times from alcohol, then from benzene, and then once or twice more from alcohol. The pure product thus obtained crystallised from boiling alcohol, in which it was easily soluble, in golden-yellow needles, m. p. 139° (yield 7 g.).

This substance, which is without odour, is readily soluble in alcohol, benzene, or glacial acetic acid. It is characterised by marked stability towards reagents. It dissolves with a dark crimson colour both in sulphuric acid and in alcoholic potash. It is hydrolysed by boiling aqueous sodium hydroxide solution, yielding *o*-toluidine. It does not react with semicarbazide, phenylcarbimide, boiling aniline or phenol, nor with sodium hypobromite solution, nor is it reduced by tin and hydrochloric acid. It is unaffected by nitrous acid, and cannot be acetylated, showing that the compound does not contain an imino-group (Found: C, 74·3; H, 5·9; N, 6·3. $C_{14}H_{13}O_2N$ requires C, 74·0; H, 5·7; N, 6·2%).

It is evident from these results that the triazole first formed loses two atoms of nitrogen during the heating, thus becoming converted into *o-tolyl*cyclo*iminotoluquinone.*

This is confirmed by the results of analyses of similar substances obtained by condensing other aromatic azides with toluquinone.

Condensation of Other Azides with Toluquinone.—Other azides condense similarly when their solutions in dry benzene are boiled with toluquinone, but as a rule only the *cyclo*iminotoluquinones can

be isolated in a pure state owing to the instability of the corresponding aziminotoluquinones. They all separate from benzene or alcohol, in which they are moderately easily soluble, in small, yellow plates or needles.

p-*Chlorophenyl*cyclo*iminotoluquinone*, m. p. 180° (Found: Cl, 14·2. $C_{13}H_{10}O_2NCl$ requires Cl, 14·32%); 2 : 4-*dichlorophenyl*cyclo*iminotoluquinone*, m. p. 209·5° (Found: Cl, 25·2. $C_{13}H_9O_2NCl_2$ requires Cl, 25·15%); 2 : 5-*dichlorophenyl*cyclo*iminotoluquinone*, m. p. 229° (Found: Cl, 25·0%); p-*bromophenyl*cyclo*iminotoluquinone*, m. p. 185° (Found: Br, 27·1. $C_{13}H_{10}O_2NBr$ requires Br, 27·4%); 2 : 4-*dibromophenyl*cyclo*iminotoluquinone*, m. p. 216° (Found: Br, 43·1. $C_{13}H_9O_2NBr_2$ requires Br, 43·2%); 2 : 4 : 6-*tribromophenyl*cyclo*iminotoluquinone*, m. p. 171° (Found: Br, 53·7. $C_{13}H_8O_2NBr_3$ requires Br, 53·2%).

THE QUEEN'S, AND KEBLE COLLEGES, OXFORD.

[*Received, March 16th*, 1925.]

CLXXIX.—*Compounds of Tervalent Molybdenum. Part III. New Oxalates.*

By WILLIAM WARDLAW and WILLIAM HENRY PARKER.

OF the metals chromium, molybdenum, tungsten, and uranium, only chromium has so far yielded oxalates of the tervalent element. This metal forms a hydrated normal oxalate, $Cr_2(C_2O_4)_3,xH_2O$, and complex salts of the types $R_2[Cr_2(C_2O_4)_4]$, $R_4[Cr_2(C_2O_4)_4(OH)_2]$, and $R_3[Cr(C_2O_4)_3]$; the potassium derivative of the last type has been resolved into its optically active components. Chilesotti (*Z. Elektrochem.*, 1906, **12**, 146), by electrolysis of a 3·5% solution of molybdenum trioxide in 2*N*-oxalic acid in a diaphragm cell, obtained an intensely yellowish-brown cathode liquid which, on concentration, with or without the addition of alkali oxalates, yielded no definite compounds. During the electrolysis a red powder, insufficient for analysis, separated in the cathode chamber. Although the stage of reduction could not be estimated accurately by titration against potassium permanganate owing to the presence of oxalic acid, such approximate titrations led Chilesotti to the conclusion that in oxalic acid, as in sulphuric and hydrochloric acids, molybdenum trioxide is not reduced electrolytically to a stage lower than the tervalent. Recently, Foerster and Fricke (*Z. angew. Chem.*, 1923, **36**, 62, 458) attempted, without success, to isolate oxalates of tervalent molybdenum by dissolving in oxalic acid the hydroxide obtained by the action of ammonia on the complex salt

$K_3[MoCl_6]$, and concentrating the solution in a vacuum, alone or with addition of alkali oxalates.

In the present research, the hydroxide precipitated by the action of ammonia on the solution, containing tervalent molybdenum, produced by the electrolytic reduction of molybdenum trioxide in sulphuric acid was dissolved in oxalic acid, and the resulting solution electrolysed in a small diaphragm cell. When the cathode liquid was added to excess of pure, dry, air-free acetone, a well-defined *molybdenum oxyoxalate*, $Mo_2O(C_2O_4)_2,6H_2O$, separated. From this compound a more basic *salt*, $Mo_4O_3(C_2O_4)_3,12H_2O$, has been obtained. On exposure to the air in presence of moisture, these compounds are oxidised to the quadrivalent state, yielding bright red solutions from which, by precipitation in dry acetone, the *oxyoxalate* $MoO(C_2O_4),3H_2O$ has been obtained.

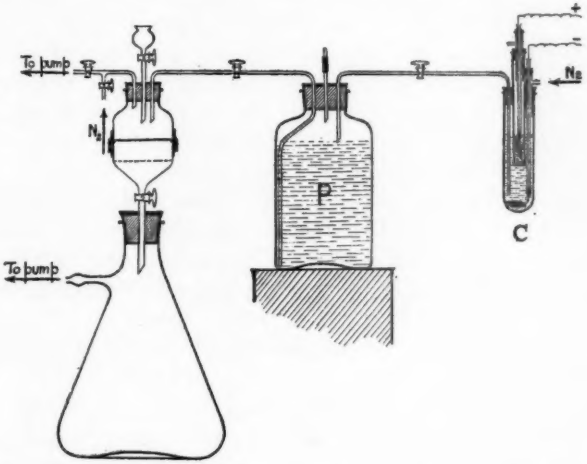
Experimental.

Preparation of the Trihydroxide.—A solution of molybdenum trioxide (40 g.) in 54 c.c. of boiling sulphuric acid (*d* 1·84) containing a few drops of nitric acid was diluted, filtered, made up to a litre, and a portion (400 c.c.) electrolysed in a diaphragm cell with smooth platinum electrodes. The solution, containing tervalent molybdenum, was forced into a flask containing 75 c.c. of ammonium hydroxide (2·5*N*), and on addition to 2 litres of hot, air-free water the hydroxide separated as a black, flocculent precipitate, which was washed free from sulphate and ammonia; a sample, dried in a vacuum, was shown to contain tervalent molybdenum (J., 1924, **125**, 1911).

Preparation of the Soluble Oxyoxalate.—Oxalic acid crystals (50 g.) were covered with water to displace air, the suspension (300 c.c.) containing all the hydroxide prepared above was added, and the whole boiled in a rapid stream of nitrogen until the volume was 100 c.c. If the volume is reduced further, hydrolysis occurs with the separation of a dark precipitate. The golden-brown solution thus produced was cooled to room temperature, when the excess of oxalic acid crystallised. The supernatant liquid was filtered, electrolysed in a small diaphragm cell, C (Fig.), the cathode chamber of which was a large boiling tube and the anode chamber a tube of smaller bore closed at the lower end by a parchment membrane. The catholyte and anolyte consisted of the same liquid and the electrolysis was conducted for 12 hours at 4 volts and a current density of 0·05 amp. per sq. cm. at the cathode. The resulting golden-brown liquid was forced by nitrogen pressure into the precipitating bottle, P, containing a litre of pure, dry, air-free acetone, when the new *oxyoxalate* separated as a

finely-divided, brown powder which rapidly became granular. This was washed with dry acetone and with dry ether, and dried, first in a rapid stream of nitrogen and finally for a short period, *in situ*, under reduced pressure. Prolonged drying in a vacuum appears to cause decomposition of the compound. During all these operations air was rigidly excluded.

Valency of the Molybdenum.—In the presence of oxalic acid it is impossible to get a satisfactory end-point when titrating reduced molybdenum solutions to the sexavalent state. The usual method for determining the valency not being available, the following procedure was adopted: A weighed quantity of the substance dissolved in air-free sulphuric acid (5*N*) was titrated in the cold



in a nitrogen atmosphere with standard permanganate. When colourless, the solution was heated to 70° and the titration continued until a permanent pink colour was obtained. This reading gives the amount of permanganate necessary to oxidise the molybdenum to the sexavalent state and to decompose the oxalate radical. The permanganate required for the latter purpose was estimated independently by warming a weighed quantity of the salt in aqueous solution with 1 c.c. of nitric acid (5*N*) and precipitating the molybdenum as MoS_3. The filtrate was freed from hydrogen sulphide by a rapid stream of carbon dioxide and titrated at 70° with permanganate. By difference—calculated for the same weight of material—the amount of permanganate required to oxidise the molybdenum to the sexavalent condition is obtained, and since 1 c.c. of *N*/10-permanganate = 0·0032 g. of Mo^{III}, the percentage of molybdenum present in the salt can be deduced.

When this agrees with the results obtained by gravimetric analysis, the molybdenum is tervalent.

0·2436 g. gave 0·1437 g. MoO_3, corresponding to 39·32% Mo. 0·2436 g. required 29·54 c.c. of $KMnO_4$, corresponding to 38·80% Mo. Therefore valency = 3.

Analysis.—The molybdenum was estimated (*a*) by direct ignition of the oxyoxalate to the trioxide, (*b*) by precipitation as MoS_3 and subsequent ignition to the trioxide. The oxalate radical was estimated as described above, and the water by ignition of the salt in dry nitrogen and absorption of the moisture in sulphuric acid [Found: (*a*) Mo, 39·3; H_2O, 21·8; (*b*) C_2O_4, 35·9. Ratio $a : b = 1 : 0·996$. $Mo_2O(C_2O_4)_2,6H_2O$ requires Mo, 39·0; H_2O, 21·95; C_2O_4, 35·8%. Ratio $a : b = 1 : 1$].

Further confirmation of this formula was obtained by heating a known amount of the salt in pure dry nitrogen to 300°. The residue thus obtained was weighed and by further ignition in air converted into the trioxide. Under these conditions, the oxyoxalate was quantitatively decomposed to give the pentoxide with evolution of carbon monoxide, which was collected and shown to be free from carbon dioxide. At a higher temperature some carbon dioxide was evolved and the residue contained a lower oxide.

0·2132 g. gave 0·1179 g. of residue (X) and 0·1248 g. of trioxide (Y). 0·2780 g. gave 0·1537 g. of residue (X) and 0·1634 g. of trioxide (Y). Ratio X/Y: Found, 0·941, 0·945; calc., 0·944.

The decomposition proceeds, therefore, in accordance with the equation $Mo_2O(C_2O_4)_2,6H_2O = Mo_2O_5 + 4CO + 6H_2O$.

Properties and Reactions.—The oxyoxalate is brown and dissolves readily in cold water to give a golden-brown solution which gradually undergoes oxidation in the air, the colour changing to bright red. Hydrolysis occurs in the slightly warmed solution with separation of a reddish-brown precipitate, probably the insoluble oxyoxalate. The new solid is very unstable in air and does not dissolve in the usual organic solvents. From the aqueous solution the oxalate radical is not precipitated by calcium chloride nor the molybdenum by alkalis in the cold, indicating the presence of a complex ion. On warming, however, a reddish-brown precipitate appears in the first case and the black hydroxide in the second. The solution has powerful reducing properties, precipitating the metal from solutions of copper and silver salts. Ferric salts are reduced to the ferrous condition. On warming with concentrated sulphuric acid the solid gives a beautiful purple solution, which on dilution with water becomes greenish-yellow and has pronounced reducing properties.

Preparation of the Insoluble Oxyoxalate.—If the electrolysis is

continued for more than 12 hours a brick-red powder gradually separates in the cathode chamber. This was noted by Chilesotti in his experiments on the electrolytic reduction of solutions of molybdenum trioxide in oxalic acid. A similar substance has now been prepared in quantity by prolonged boiling of the solution of molybdenum trihydroxide in oxalic acid. The solid was washed by decantation with air-free water and dried in the special apparatus shown in the figure after further treatment with alcohol and dry ether. Analysis by the methods already described showed the molybdenum to be tervalent, and the compound to have the formula $Mo_4O_3(C_2O_4)_3,12H_2O$ [Found: (*a*) Mo, 42·2, 41·9; (*b*) C_2O_4, 28·8, 28·8. Ratio $a : b = 1 : 0{\cdot}746$, $1 : 0{\cdot}75$. $Mo_4O_3(C_2O_4)_3,12H_2O$ requires Mo, 42·1; C_2O_4, 28·95%. Ratio $1 : 0{\cdot}75$].

During the preparation of this substance carbon dioxide and carbon monoxide were evolved from the boiling solution. The residue obtained by igniting the compound in a current of pure dry nitrogen was bluish-black and pyrophoric and on exposure to air was converted spontaneously into the pentoxide. The composition of the residue varies with the temperature of decomposition, which may occur in two main ways :—

(1) $Mo_4O_3(C_2O_4)_3 = 2Mo_2O_3 + 3CO + 3CO_2$.

(2) $Mo_4O_3(C_2O_4)_3 = 2MoO_2,Mo_2O_5 + 6CO$.

By carrying out the ignition in a short piece of combustion tubing fitted with glass taps, it was possible to weigh the pyrophoric residue, and, on admission of air, to determine the weight of Mo_2O_5 obtained from it. This gave the trioxide on further heating in air. It was hoped to obtain the sesquioxide according to equation (1), but this was found impossible. The residue obtained at 300° was Mo_4O_9 and under these conditions only carbon monoxide was evolved, the decomposition proceeding according to equation (2). At still higher temperatures, some carbon dioxide was formed and the residue varied in composition, but approximated to MoO_2, according to the reaction $Mo_4O_3(C_2O_4)_3 = 4MoO_2 + 5CO + CO_2$. The relative volumes of the gases evolved were in agreement with the residues obtained and afford a confirmation of the empirical formula deduced from analysis.

Properties and Reactions.—The pure dry product is bright reddish-brown and insoluble in water and the usual organic solvents. Hot concentrated hydrochloric acid and cold concentrated sulphuric acid dissolve it readily to give reddish-brown solutions, whilst warm dilute nitric acid produces a bright red solution which on boiling is decolorised through oxidation. A suspension of the insoluble oxyoxalate in water shows the same reducing properties as the soluble oxyoxalate. Alkalis do not dissolve it, but

change its colour to reddish-violet in the cold and black on heating.

Molybdenyl Oxalate.—The golden-brown solution prepared electrolytically undergoes gradual oxidation on exposure to the air and becomes carmine-red. If this solution is concentrated carefully on a water-bath, and the excess of oxalic acid crystallised, the filtrate yields in acetone a pinkish-red powder which on washing with alcohol and drying over phosphoric oxide contains quadrivalent molybdenum and has the composition $MoO(C_2O_4),3H_2O$. Its formation under these conditions may be represented thus: $Mo_2O(C_2O_4)_2 + \frac{1}{2}O_2 + H_2O = 2MoO(C_2O_4) + H_2O$. This is comparable with the transformation of the double cyanide, $K_3[Mo(CN)_6]$, of tervalent molybdenum, to $K_4[Mo(CN)_8]$, containing quadrivalent molybdenum, by air oxidation in the presence of water in accordance with the equation $K_3[MoCl_6] + \frac{1}{2}O_2 + \frac{1}{2}H_2O + 8KCN = K_4[Mo(CN)_8] + 6KCl + KOH$. Owing to the complete solubility of this oxalate in water without decomposition the molybdenum could be precipitated quantitatively from the hot solution by potassium hydroxide as the black hydroxide, which was weighed as MoO_3 after ignition in air. The oxalate radical was estimated in the acidified filtrate by titration with permanganate. The molybdenum was also determined by direct ignition of the oxalate to the trioxide [Found: (*a*) Mo, 37·75; (*b*) C_2O_4, 34·7; H_2O, 21·0. Ratio $a : b$ = 1 : 0·996. $MoOC_2O_4,3H_2O$ requires Mo, 37·8; C_2O_4, 34·65; H_2O, 21·3%. Ratio 1 : 1].

By ignition of the compound in a current of pure dry nitrogen a black residue corresponding to the dioxide was obtained, the decomposition proceeding according to the equation $MoOC_2O_4 = MoO_2 + CO + CO_2$ [0·0932 g. of residue (X) gave 0·1048 g. of MoO_3 (Y). Ratio X : Y, found 0·890; calc., 0·889].

Properties of Molybdenyl Oxalate.—The red powder as prepared above is extremely hygroscopic, and very soluble in water, producing a magenta-coloured solution which appears quite stable in the air. From the freshly-prepared solution, which has a pronounced acid reaction, the oxalate radical is not precipitated by calcium chloride nor the molybdenum by alkalis in the cold, which render the solution bluer. The presence of a complex ion in this oxalate of quadrivalent molybdenum, together with its acidic properties and the colour changes produced by alkalis, suggests its formulation as $\left[Mo\begin{matrix}O_2\\2H_2O\end{matrix}C_2O_4\right]H_2$.

Experiments now in progress indicate the existence of two salts corresponding to this dibasic acid. The aqueous solution slowly deposits silver and copper from solutions of their salts, whilst ferric

salts are immediately reduced to the ferrous condition. These reducing properties are not so pronounced as those of the oxalates of tervalent molybdenum.

Conclusion.

So far, no compound of molybdenum is known certainly to produce a tervalent molybdenum ion. The new soluble oxyoxalate shows remarkable similarity in its properties and mode of decomposition to the oxysulphate previously described (J., 1924, **125**, 1910).

$Mo_2O(SO_4)_2,6H_2O = Mo_2O_5 + 2SO_2 + 6H_2O.$

$Mo_2O(C_2O_4)_2,6H_2O = Mo_2O_5 + 4CO + 6H_2O.$

In both these compounds, the molybdenum is present as a complex ion and they may be represented by the formulæ

$3H_2O{\cdot}XO_4{\cdot}Mo{\cdot}O{\cdot}Mo{\cdot}XO_4{\cdot}3H_2O$ or $\left[3H_2O{\cdot}Mo\begin{matrix}XO_4\\ O\\ XO_4\end{matrix}Mo{\cdot}3H_2O\right]$,

where $XO_4 = SO_4$ or C_2O_4. A further possibility would be to consider these substances as dibasic acids of the formula $\left[Mo\begin{matrix}O\\ 3H_2O\end{matrix}XO_4\right]_2H_2$. The ease with which they hydrolyse and oxidise in aqueous solution renders conductivity measurements of little significance. There seems to exist a distinct analogy between the chromium salt, $2R_2C_2O_4,Cr_2(C_2O_4)_2(OH)_2$, and the new oxyoxalate, $Mo_2O(C_2O_4)_2$. Werner (*Annalen*, 1914, **406**, 261) assigned to this double chromium oxalate the constitution

$$\left[(C_2O_4)_2Cr\begin{matrix}OH\\ OH\end{matrix}Cr(C_2O_4)_2\right]R_4,$$

of which the free acid would be $\left[(C_2O_4)_2Cr\begin{matrix}OH\\ OH\end{matrix}Cr(C_2O_4)_2\right]H_4$. Owing probably to its great instability, this substance has not been isolated, but a probable decomposition product would be the analogue of the molybdenum oxyoxalate,

$$\left[2H_2O(C_2O_4)Cr\begin{matrix}OH\\ OH\end{matrix}Cr(C_2O_4)2H_2O\right].$$

In this formula, only five molecules of water are represented in the co-ordination sphere. The formation of the insoluble oxyoxalate from the soluble salt by warming its aqueous solution takes place with separation of oxalic acid, detected by its ionic reactions. This change may be symbolised as follows:

$$2Mo_2O(C_2O_4)_2 + H_2O = Mo_4O_3(C_2O_4)_3 + H_2C_2O_4.$$

The relationship which exists between the new oxalate of quadrivalent molybdenum and the known derivatives of the quinque- and sexa-valent element is clearly seen from the co-ordination

formulæ for these substances. The compounds of sexavalent molybdenum comprise the free acid and its salts,

$$\left[\mathrm{Mo}\begin{matrix}\mathrm{O_3}\\ \mathrm{C_2O_4}\end{matrix}\right]\mathrm{H_2},\ \mathrm{R'H},\ \mathrm{R'_2}.$$

The derivatives of the quinquevalent element are known only as salts, $\left[\mathrm{Mo}\begin{matrix}\mathrm{O_2}\\ \mathrm{C_2O_4}\end{matrix}\right]\mathrm{R'}$, whilst the oxalate of quadrivalent molybdenum now prepared is probably $\left[\mathrm{Mo}\begin{matrix}\mathrm{O_2}\\ \mathrm{C_2O_4}\ 2\mathrm{H_2O}\end{matrix}\right]\mathrm{H_2}$.

Summary.

(1) By electrolytic reduction of a solution of the trihydroxide of molybdenum in oxalic acid and precipitation in acetone an oxyoxalate of tervalent molybdenum, $\mathrm{Mo_2O(C_2O_4)_2,6H_2O}$, has been obtained.

(2) Decomposition of the above oxalate or prolonged boiling of a solution of the trihydroxide in oxalic acid yields the insoluble oxyoxalate, $\mathrm{Mo_4O_3(C_2O_4)_3,12H_2O}$.

(3) Air oxidation of these compounds in presence of water yields a red solution which gives with alcohol a precipitate of molybdenyl oxalate, $\mathrm{MoO(C_2O_4),3H_2O}$, and is being further studied.

(4) The oxalate radical is present as a complex ion.

The authors wish to express their thanks to Messrs. Brunner Mond and Co., Ltd., for a grant which has defrayed the cost of the apparatus.

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[*Received, March 24th*, 1925.]

CLXXX.—*Bromination of* 4′-*Amino*-1-*phenyl*-5-*methylbenzthiazole and of* 1 : 1-*Bisbenzthiazole.*

By ROBERT FERGUS HUNTER.

THE dibromo-addition compound formed from dehydrothiotoluidine (4′-amino-1-phenyl-5-methylbenzthiazole) by bromination in glacial acetic acid (Gattermann, *Ber.*, 1889, **22**, 422) cannot have the constitution $\mathrm{C_6H_3Me}\begin{matrix}\mathrm{S}\text{---}\\ \mathrm{NBr}\end{matrix}\!>\!\mathrm{CBr{\cdot}C_6H_4{\cdot}NH_2}$, for it lacks the explosive properties normally associated with the presence of the group :NBr (Spencer, this vol., p. 216) and is relatively stable to air, boiling water, dilute alkalis, etc. Since the action of sulphurous acid or sodium hydrogen sulphite instantly reconverts it into dehydrothiotoluidine, hydrogen bromide being evolved, the com-

pound is a perbromide, although of unusual stability, the most probable constitution being $C_6H_3Me<\overset{S}{\underset{NBr_2}{}}>C\cdot C_6H_4\cdot NH_2$.

Similarly, the *tetrabromo*-addition compound of 1 : 1-bisbenzthiazole and bromine is a perbromide, probably of the constitution $C_6H_4<\overset{S}{\underset{NBr_2}{}}>C\cdot C<\overset{S}{\underset{NBr_2}{}}>C_6H_4$, for it also is instantaneously reduced to the parent bisbenzthiazole on treatment with sulphurous acid; moreover, it loses its bromine on mere exposure to the air or in boiling alcohol containing a trace of alkali.

EXPERIMENTAL.

In the preparation of 4′-amino-1-phenyl-5-methylbenzthiazole a mixture of alcohol and benzene (1 : 1) is a much better solvent than the alcohol and acetone formerly used (*J. Soc. Chem. Ind.*, 1923, **42**, 302).

In the preparation of the dibromide the acetic acid (Gatterman, *loc. cit.*) was replaced by chloroform, from which the dibromide separated in dark red-brown granules, which were dried in a vacuum over potassium hydroxide; m. p. 190° (sintering). Yield quantitative. The dibromide cannot be diazotised, treatment with nitrous acid causing evolution of bromine and production of highly resinous products.

1 : 1-*Bisbenzthiazole.*—1-Chlorobenzthiazole (Hofmann, *Ber.*, 1879, **12**, 1126) was recovered unchanged after being heated under reflux with sodium in dry ether.

A mixture of acetanilide and sulphur (Hofmann, *Ber.*, 1880, **13**, 1223) was heated at its b. p. for 30 hours, pale yellow needles of bisbenzthiazole subliming. The product was extracted with 60% sulphuric acid (Lauth, *Bull. Soc. chim.*, 1896, **15**, 82), and the crude base heated under reflux with alcohol. Sublimation of the base, although yielding a pure product, involves very heavy losses due to carbonisation. The compound is very sparingly soluble in all ordinary solvents and in nitrobenzene or aniline, but dissolves readily in tetrachloroethane. Purification by crystallisation from alcohol is quite ineffective, although described in the original paper (*loc. cit.*). The substance crystallises from absolute alcohol–tetrachloroethane in fine, colourless crystals which do not melt below 300°.

Bromination.—The base was recovered unchanged after treatment in alcoholic suspension with excess of bromine.

The bisbenzthiazole (2 g.) suspended in 40 c.c. of chloroform was slowly treated with 4 c.c. of bromine; after ½ hour the mixture was warmed on a water-bath, when the bulk of the solid dissolved. The

solution was filtered, concentrated, and cooled; on scratching, red-brown needles of the *tetrabromide* separated which were dried on a porous tile in a vacuum. It becomes pale yellow and loses bromine at about 170°, but the actual melting point appears to be above 300° (Found: Br, 52·9. $C_{14}H_8N_2Br_4S_2$ requires Br, 54·5%). The tetrabromide loses bromine while it is being weighed.

In conclusion the author desires to express his gratitude to Prof. J. F. Thorpe and Dr. M. A. Whiteley for their kind interest in this work.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
LONDON, S.W. 7. [*Received, April 25th*, 1925.]

CLXXXI.—*The Decomposition of Hydrogen Peroxide by Cobaltic Hydroxide.*

By FREDERICK GERALD TRYHORN and GILBERT JESSOP.

HYDROGEN peroxide is very slowly decomposed in neutral solution by a suspension of cobaltic hydroxide. Traces of alkali, of themselves too small to cause decomposition, greatly increase the activity of the hydroxide. Velocity coefficients for such a reaction calculated on the basis of a monomolecular decomposition of the peroxide are unsatisfactory. Thus Bredig and his collaborators (*Z. physikal. Chem.*, 1899, **37**, 258; *Ber.*, 1904, **37**, 798), using cobalt hydroxide and colloidal platinum, found a steady rise of the constant in the presence of alkali, for which no satisfactory explanation has been offered. Occasion arose to investigate further this reaction, since the catalase-like action of many cobaltammine salts in decomposing hydrogen peroxide (Shibata and Kaneko, *J. Chem. Soc. Japan*, 1923, **44**, 166) has been found to be due to cobaltic hydroxide produced by slow hydrolysis of the cobaltammine ions.

EXPERIMENTAL.

The decomposition of the hydrogen peroxide was followed by determining the rate of evolution of oxygen at constant pressure. Reaction occurred in a glass bulb of about 40 c.c. capacity which could be connected by a three-way tap to either of two 5-c.c. gas burettes provided with levelling bulbs and calibrated gravimetrically. By these means oxygen collected in one burette could be measured accurately while the other burette was filling. During the experiments, in all of which Merck's " perhidrol " (unstabilised), freshly diluted with conductivity water and estimated by titration,

was used, the bulb was vigorously agitated by means of a motor, and the whole of the apparatus was immersed in a thermostat at $25 \pm 0{\cdot}02°$. In one or two series of experiments in which readings were required at long time intervals the titration method was used.

Cobaltic hydroxide was prepared by the addition of ammonia to a mixture of hydrogen peroxide and cobalt chloride solution. Suitably low concentrations of these reagents gave a stable brown sol; higher concentrations gave unstable sols which soon coagulated. In these cases, the hydroxide was shaken into a coarse suspension and used as such. In all but the preliminary experiments, for reasons referred to later, the catalyst preparations were treated with an excess of hydrogen peroxide before use. Some comparison experiments were made with a suspension of cobalt peroxide prepared by Howell's method (*Proc. Roy. Soc.*, 1923, *A*, **104**, 134). This was unstable in presence of hydrogen peroxide, changing immediately from black to the characteristic brown colour of the cobaltic hydroxide preparations, and showing the catalytic behaviour of these.

Table I gives the reactant concentrations in the experiments quoted. All concentrations are expressed in millimoles per litre of reaction mixture. The letters *a*, *b*, *c*, indicate successive additions of hydrogen peroxide to the same reaction mixture.

Results.

The treatment of the results has been based on the equation for a catalysed monomolecular reaction, $dx/dt = kA(a - x)$. Integration over a small time interval, during which the activity of the catalyst may be regarded as constant, gives

$$kA = 1/(t_2 - t_1) \,.\, \log \{(a - x_1)/(a - x_2)\},$$

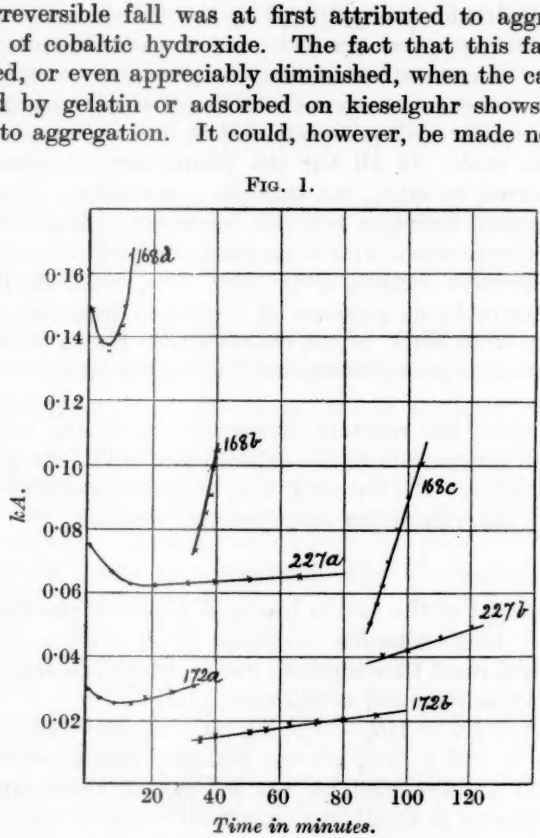
where $a - x_1$ and $a - x_2$ are the reactant concentrations at the times t_1 and t_2. Provided, as was the case in these experiments, the time interval is small, the calculated value of kA, which has been used as a measure of the catalyst activity, becomes very nearly the true value at the mean time $(t_2 + t_1)/2$.

The curves in Fig. 1, for some preliminary experiments, indicate the changes in activity of a given mass of catalyst. In these experiments, two or more portions of hydrogen peroxide were decomposed successively in presence of traces of ammonia by one portion of catalyst, the second portion of peroxide being added as soon as the first reaction had ceased. During the first part of each experiment the activity fell, passed through a minimum, and then rose, either rapidly or slowly. In the latter parts of the experiments the initial fall of activity was absent, the new curve lying below the previous one, and showing a rise of activity as the

hydrogen peroxide concentration decreased. The activity appears subject to a dual change: an irreversible fall, and a simultaneous reversible increase inversely dependent on the hydrogen peroxide concentration.

The irreversible fall was at first attributed to aggregation of particles of cobaltic hydroxide. The fact that this fall was not eliminated, or even appreciably diminished, when the catalyst was protected by gelatin or adsorbed on kieselguhr shows that it is not due to aggregation. It could, however, be made negligible in

FIG. 1.

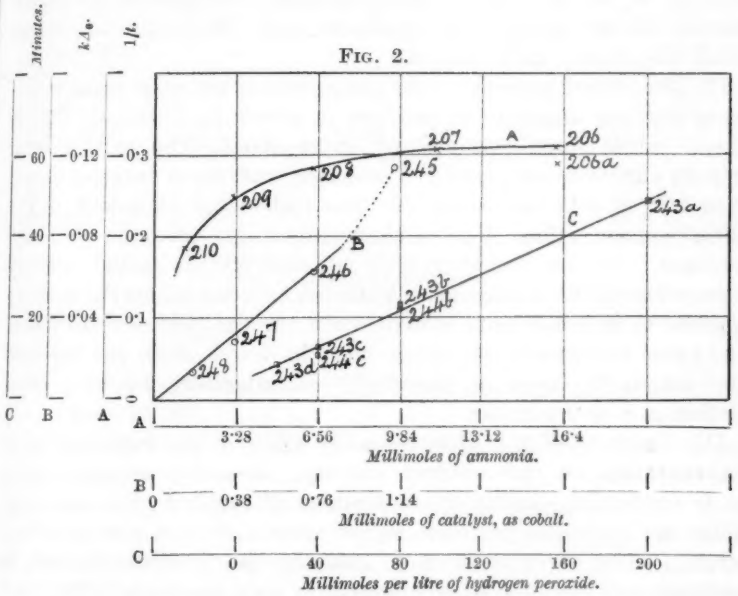


two ways; by treating the catalyst with excess of hydrogen peroxide, or by allowing it to form very slowly by the hydrolysis of a cobaltammine salt.

These facts suggest that the irreversible fall in activity is due to a change in the nature of the catalyst surface. When the hydroxide particles are formed as the result of a sudden molecular condensation, it may happen that the surface molecules are deposited at so rapid a rate that they do not orient themselves in positions of minimum potential energy. If during catalysis such a surface adsorbs hydrogen peroxide, the operation of the adsorptive forces may so disturb or weaken the cohesive forces binding the cobaltic

hydroxide molecules together that on decomposition of the peroxide the loosened hydroxide can rearrange itself on the surface in a position of minimum potential energy. If, as seems likely, the stable orientation of the surface molecules corresponds with a minimum activity, the catalyst will suffer an irreversible fall of activity to a value constant for a given hydrogen peroxide concentration. When, on the other hand, the hydroxide aggregates are formed as a result of a slow hydrolytic process, each molecule will be deposited in a position of minimum potential energy, and the irreversible fall of activity should be absent, in agreement with experiment.

FIG. 2.



Though the forms of the curves in Fig. 1 were easily reproducible, similar experiments were not reproducible numerically to within less than about 5%. This difficulty was overcome by treating the catalyst preparation with excess of hydrogen peroxide to prevent the irreversible fall of activity. Reproducibility to within 2% was thus secured. Catalyst so treated was then used to investigate the effect of varying individually the amounts of catalyst, ammonia, and hydrogen peroxide in the reaction, with the following results.

I. Curve A, Fig. 2, shows the influence of small amounts of ammonia on the catalytic decomposition of hydrogen peroxide by a fixed amount of catalyst. To make the results comparable, the reciprocals of the time of evolution of 20 c.c. of oxygen (at 25°

and 760 mm. pressure) are plotted against ammonia concentrations. The ordinates are thus measures of the catalyst activity during a fixed portion of the reaction. The activity is increased on addition of ammonia, rapidly at first and then slowly towards a constant value. Check experiments without catalyst showed that the highest ammonia concentrations used in this series produced no measurable decomposition of the peroxide during the period of an experiment. This promoter effect is attributable to the influence of hydroxyl ions, since by adding ammonium chloride to repress the ionisation of the ammonium hydroxide the activity of the catalyst was sharply depressed. At still higher ammonia concentrations, a fall of activity was indicated, attributable to partial solution of the catalyst, in agreement with the results of Clarens (*Bull. Soc. chim.*, 1923, **33**, 280).

II. The initial activity of the catalyst in a series of experiments using varying amounts of catalyst is shown in curve B, Fig. 2. These values were obtained by extrapolating the experimental activity curves to zero time. The concentrations of catalyst varied from 1·12 to 0·19 millimoles per litre (calculated as cobalt). The initial concentrations of ammonia and hydrogen peroxide were kept constant. At low concentrations of catalyst the initial activity is proportional to its amount. At higher concentrations the activity appears to increase more rapidly than the catalyst concentration. The value for experiment 245 is open to doubt, since the reaction was extremely rapid in this high concentration, reaching completion in 8 or 9 minutes.

III. Curve C, Fig. 2, illustrates the effect of hydrogen peroxide concentration on the catalyst activity. Reaction mixtures were made containing similar concentrations of catalyst and ammonia, while the hydrogen peroxide varied over a tenfold concentration range. These experiments were made by the titration method, as readings were required at comparatively long intervals. The time necessary for a 10% decomposition of the hydrogen peroxide was taken as a measure of the catalyst activity. The catalyst activity varies inversely as the time of decomposition of a given portion of the peroxide. From the curve the activity may be seen to be an inverse linear function of the initial hydrogen peroxide concentration.

Discussion.

Freundlich ("Kapillarchemie," 380 *et seq.*) attributed the rise of activity of colloidal platinum in decomposing hydrogen peroxide to the change of the hydroxyl-ion concentration during reaction. An investigation of this suggestion has shown that the rise of activity persisted in reaction mixtures in which the hydroxyl-ion concen-

TABLE I.

Experiment.	Catalyst (as cobalt).	Ammonia.	Ammonium chloride.	Hydrogen peroxide.
168*a*, *b*, *c*.	0·133	6·54	0·266	63·6, 62·3, 59·8
172*a*, *b*.	0·0533	6·54	0·1066	65·0, 68·0
173*b*, 174*b*.	0·12	6·54	0·24	60·5, 76·5
175*b*.	0·133	6·54	0·266	74·8
197*b*.	0·28	11·45	0·56	55·8
206, 207.	—	16·40, 11·48	—	62·5, 62·1
208, 209.	0·14	6·56, 3·28	0·28	62·2, 62·4
210, 227*a*.	—	1·13, 16·40	—	61·7, 71·7
227*b*.	—	16·40	—	54·6
231*b*, 235*a*.	0·28	16·40, 13·12	17·23	47·7, 65·5
235*b*, 235*c*.	—	13·12, 16·40	—	65·6, 64·1
238*b*.	0·28	6·54	0·56	65·8
240*b*, 241*b*.	0·28	16·40	16·40	66·3, 62·3
243*a*, 243*b*.	0·056	16·40	16·40	170·7, 85·3
243*c*, 243*d*.	—	—	—	41·0, 20·3
244*b*, 244*c*.	—	—	—	85·3, 41·0
245, 246.	1·12, 0·75	16·40	16·40	65·7, 66·1
247, 248.	0·373, 0·19	—	—	69·3, 68·3
249*b*, 250*b*.	CoO_2 Platinum catalyst.	16·40	16·40	41·7, 52·3
251.	0·0194	—	—	60·4
252*a*, *b*, *c*.	0·0485	—	—	57·0, 51·7, 54·1
263*a*, *b*.	0·0383	—	—	65·0, 67·1
	Palladium catalyst.	NaOH (Bredig and Fortner).		
VII	0·001	0·003	—	100·0
VIII, IX	0·064, 0·016	16·0	—	100·0
X	0·004	—	—	—

tration was made constant by Washburn's method (*J. Amer. Chem. Soc.*, 1908, **30**, 37).

It was not found possible to interpret the observed facts by any purely chemical mechanism of reaction. The more probable mechanism is that the decomposition of the peroxide occurs in an adsorbed film at the cobalt hydroxide surface. Application of Freundlich's adsorption equation requires a linear relation between $\log 1/kA$ and $\log (a - x)$. Whilst this relationship held over some portion of many reactions, in no case was it applicable to a complete reaction.

The use of the Freundlich equation implies that there is no upper limit to the amount of hydrogen peroxide adsorbable by a given amount of cobaltic hydroxide. This leads to the conclusion that in any but extremely weak solutions the adsorbed film must be many molecules in thickness. Langmuir has adduced evidence (*Trans. Faraday Soc.*, 1922, **17**, 607) that the surface attractive forces are operative only over distances of the order of atomic diameters, and that adsorption ceases after the formation of a monomolecular layer. A treatment of the present results on this basis by the method used by Langmuir (*loc. cit.*, p. 621) has proved

more satisfactory. The following mechanism is therefore suggested for the reaction.

Adsorption of hydrogen peroxide molecules on the catalyst surface, at a rate proportional to their concentration in the reaction mixture, causes a redistribution of the intramolecular force fields in the adsorbed molecules, resulting in an increased tendency to ionise of one hydrogen atom. This may be visualised as due to a dragging of the electron sheaths of the oxygen atoms towards the adsorbing surface with the result that the repulsion between the oxygen nuclei and hydrogen nuclei is enhanced. This "loosened" hydrogen ion is then removed as water on the impact of a hydroxyl ion, leaving the unstable ion O_2H' adsorbed on the surface. This mechanism accounts in a simple way for the form of curve A, Fig. 2. The average life of an adsorbed hydrogen peroxide molecule in low hydroxyl-ion concentrations may be comparatively long; addition of alkali increases the rate of collision of hydroxyl ions with adsorbed peroxide molecules, the average life of which is thereby shortened. This will approach to a minimum value when so much alkali has been added that the rates of impact of hydroxyl ions and of adsorption of peroxide molecules are equal. Increase of alkali beyond this limit will be without further effect unless dissolution of the catalyst is caused. The O_2H' ions left on the catalyst are unstable and decompose, regenerating hydroxyl ions and leaving atomic oxygen on the surface. If, as seems probable, the tendency for atomic oxygen to revert to the molecular form is greater than its tendency to form an adsorption complex with the catalyst, molecular oxygen will be formed. This mechanism may be represented graphically thus :—

$$S:::O=O<\begin{matrix}H\\H\end{matrix} + OH' \longrightarrow S:::O=O<\begin{matrix}\\H'\end{matrix} + H_2O \longrightarrow S + \tfrac{1}{2}O_2 + OH'$$

where S indicates the catalyst surface.

The portion of the catalyst surface concerned in the above changes is to be regarded as the active surface. This is not necessarily the whole of the surface. If the possibility of selective adsorption is admitted, a large part of the total surface must be considered as occupied by water molecules. Since the concentration of these does not appreciably change during reaction, the surface so occupied, and also the active surface, may be regarded as constant.

The active surface at any moment may be regarded as partly free and partly occupied by peroxide molecules and ions. If θ_1, θ_2, represent the fractions of the active surface which are occupied by peroxide molecules and ions, and θ_3 the free active surface, then

$$\theta_1 + \theta_2 + \theta_3 = 1 \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Assuming that the rates of impact of peroxide molecules and of hydroxyl ions on unit surface of the catalyst are proportional to their concentrations in solution, we may write the following expressions for "rates of reaction" per unit area of the catalyst surface,

Rate of condensation of peroxide molecules $= \alpha_1 c_1$
Rate of decomposition of adsorbed molecules $= \alpha_2 c_2$
Rate of decomposition of peroxide ions $= \alpha_3$

where α_1, α_2, α_3 are constants and c_1 and c_2 are the concentrations of hydrogen peroxide and hydroxyl ions in solution. For a steady state the actual rates of the above reactions are equal and

$$\alpha_1\theta_3 c_1 = \alpha_2 c_2 \theta_1 = \alpha_3 \theta_2 \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Here, $\alpha_3\theta_2$ is the rate of formation of atomic oxygen per unit active surface. If the polymerisation of this to molecular oxygen is regarded as instantaneous, the corresponding rate of evolution of gaseous oxygen is $\frac{1}{2}\alpha_3\theta_2$. For a catalyst of total active surface S the observed rate of reaction becomes $\frac{1}{2}S\alpha_3\theta_2 = dx/dt$. Eliminating θ_1, θ_3 in (1) by means of (2) and writing

$$\alpha_3\theta_2 = \frac{2dx/dt}{S}, \text{ we get } \frac{2}{S}\frac{dx}{dt}\left[\frac{1}{\alpha_1 c_1} + \frac{1}{\alpha_3} + \frac{1}{\alpha_2 c_2}\right] = 1.$$

For c_1 we may write $(a - x)$ and so obtain

$$\frac{(a-x)}{dx/dt} = \frac{1}{kA} = \frac{2}{S}\left[(a-x)\left\{\frac{1}{\alpha_2 c_2} + \frac{1}{\alpha_3}\right\} + \frac{1}{\alpha_1}\right] \quad . \quad . \quad (3)$$

This equation may be tested in several ways.

A. The rise in the ordinary monomolecular velocity coefficient is accounted for by the fact that it is measured by the term $1/(a - x) \,.\, dx/dt$. According to the mechanism suggested above, the value of dx/dt will remain constant so long as there is present sufficient hydrogen peroxide to maintain the adsorption equilibrium, although the value of $(a - x)$ is steadily decreasing. Thus the value of $1/(a - x) \,.\, dx/dt$ will increase.

B. In any given experiment in which S and c_2 are constant, equation (3) reduces to

$$1/kA = k_1(a - x) + k_2 \quad . \quad . \quad . \quad . \quad (4)$$

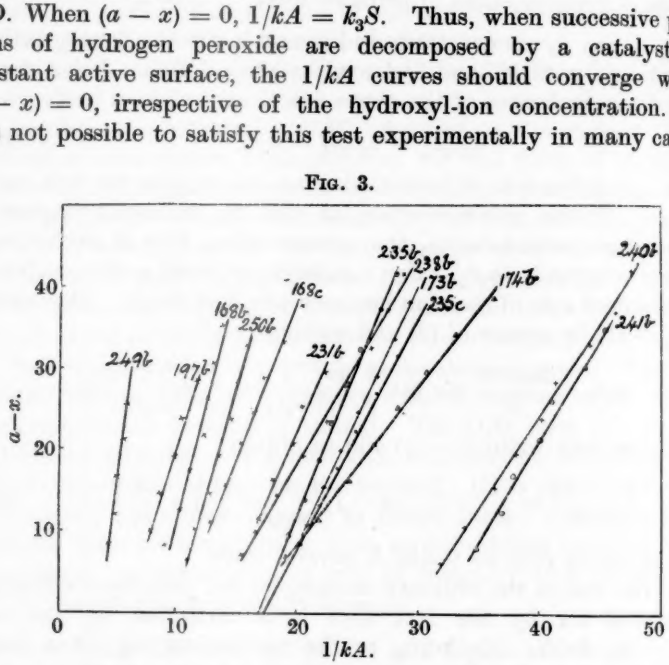
Thus $1/kA$ should be a linear function of $(a - x)$. We may regard c_2, the hydroxyl-ion concentration, as constant so long as it lies in the region where further increase is without effect on the catalyst, or in experiments in which it is regulated by the addition of ammonium chloride. Fig. 3 illustrates the application of this test to a number of experiments in which these conditions held, and in which the irreversible fall in activity had been eliminated

by previous treatment of the catalyst with hydrogen peroxide. In every case a satisfactory linear relation is obtained.

C. The form of curve A, Fig. 2, follows from equation (3), if the concentration of hydroxyl ions in very dilute ammonia solutions is regarded as proportional to the ammonia concentration; for, when S and $(a - x)$ are constant, (3) reduces to $kA = nc_2/(1 + mc_2)$, where n and m are constants.

D. When $(a - x) = 0$, $1/kA = k_3S$. Thus, when successive portions of hydrogen peroxide are decomposed by a catalyst of constant active surface, the $1/kA$ curves should converge when $(a - x) = 0$, irrespective of the hydroxyl-ion concentration. It was not possible to satisfy this test experimentally in many cases,

FIG. 3.



since any slight aggregation or surface change in the catalyst will greatly affect the convergence points of the curves. Fig. 3 includes one pair of experiments (235*b*, 235*c*) in which the necessary conditions were fulfilled. This test seems easier to realise in the case of catalysis by colloidal platinum (experiments 252*a*, *b*, *c*, Fig. 4). This is to be expected, since surface changes are less probable when dealing with metal particles.

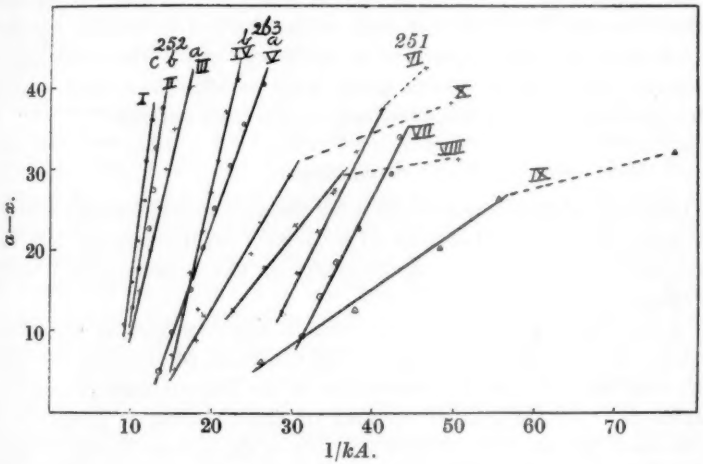
E. When $(a - x)$ and c_2 are constant, equation (3) reduces to $1/kA = k_4/S$—or, in experiments with constant hydrogen peroxide and ammonia concentrations, the initial activity should be proportional to the active surface, and therefore to the amount, of catalyst. This relationship is realised for low concentrations of catalyst in curve B, Fig. 2.

Since the mechanism suggested for the present reaction is inde-

pendent of the chemical nature of the catalyst, equation (4) was further tested by applying it to some data of Bredig and Fortner (*Ber.*, 1904, **37**, 798) for the decomposition of hydrogen peroxide by alkaline palladium sol. Monomolecular velocity coefficients calculated by them showed a rise, in many cases as much as 25%, during the reaction.

Curves VII—X, Fig. 4, refer to some of these experiments, in which the reactant concentrations were those given in Table I. To bring these curves into suitable positions in Fig. 4, the actual values of $(a - x)$ have been multiplied by 5, and the values of $1/kA$ divided by 20, 5, 2, and 2, respectively. Except in the initial stages of the reactions, equation (4) applies with reasonable accuracy.

FIG. 4.



The other curves in Fig. 4 are for some experiments which were made with colloidal platinum. This was prepared by reducing platinum chloride solution with formaldehyde and dialysing. The composition of the reaction mixtures is given in Table I. The monomolecular velocity coefficients for these experiments showed a steady rise during the course of the reaction, and a very considerable deviation from the linear relation required by the Freundlich equation was found on plotting $\log kA$ against $\log (a - x)$. Application of equation (4) leads to satisfactory results (Curves I—VI, Fig. 4).

Reference may be made here to Maxted's results for the poisoning of platinum catalysts by mercuric chloride (J., 1922, **121**, 1760). In the decomposition of hydrogen peroxide, the poisoning of the platinum was, over a fairly wide range, proportional to the

amount of mercury salt added. On the assumption that the poisoning is due to selective adsorption of mercury, the amount of active surface thus occupied will be a measure of the poisoning action, if the decomposition of the peroxide occurs at the catalyst surface. From equation (3) the catalyst activity is proportional to the surface available for hydrogen peroxide adsorption : a linear decrease of this surface due to mercury adsorption thus corresponds to a similar decrease in activity.

The mechanism suggested in this paper may be applied to account for the varying activities shown by different substances in catalysing the decomposition of hydrogen peroxide. The activity of a surface in this respect will depend on the magnitude of its stray force fields. These will determine the extent of disturbance of the intramolecular force fields in adsorbed hydrogen peroxide molecules, and therefore the ease with which a hydrogen ion may be removed by the impact of a hydroxyl ion. The stability of hydrogen peroxide in vessels lined with paraffin wax may thus be attributed to the non-polar nature of the wax surface.

Summary.

Cobaltic hydroxide as a catalyst for the decomposition of hydrogen peroxide shows a dual change of activity; an irreversible fall, and a reversible increase varying inversely as the concentration of the peroxide.

By varying separately each factor in the reaction, it was found that (*a*) the apparent activity of a given mass of catalyst increases with addition of traces of ammonia to an approximately constant maximum; (*b*) the initial activity of the catalyst is proportional to its amount; (*c*) the catalyst activity is an inverse linear function of the hydrogen peroxide concentration.

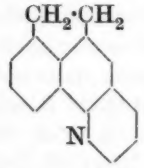
A mechanism is suggested for the reaction in which the decomposition of the peroxide occurs in a monomolecular film on the catalyst surface, a distortion of the intramolecular force field on adsorption rendering one hydrogen atom of the peroxide molecule removable by the impact of a hydroxyl ion. The peroxide ion thus formed decomposes to give oxygen and hydroxyl ions. An equation derived on this basis is shown to agree with experimental data, and to be applicable to other cases of catalysis.

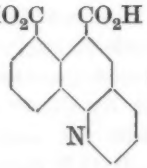
UNIVERSITY OF SHEFFIELD. [*Received, March 19th*, 1925.]

CLXXXII.—α-*Acenaphthaquinoline.*

By JESSIE STEWART.

WHEN 5-aminoacenaphthene is allowed to undergo Skraup's reaction under conditions analogous to those employed by Bamberger and Stettenheimer (*Ber.*, 1891, **24**, 2474) in the preparation of α-naphthaquinoline, there results a *base* of melting point 61—62° (I). On oxidation with chromic acid it gives *α-naphthaquinoline-6 : 7-dicarboxylic acid* (II), which when heated with soda-lime is readily converted into α-naphthaquinoline.

(I.) 

(II.) 

α-Acenaphthaquinoline (I).—A mixture of 10 g. of 5-aminoacenaphthene (*Ber.*, 1911, **44**, 2855), 5 g. of nitrobenzene, 18 g. of glycerol, and 8 c.c. of concentrated sulphuric acid was heated under reflux, at first very gently and finally at 150—160° for 3—4 hours. The product, while still hot, was poured into water (4 vols.). The chromate of the base (yield 10 g.), isolated exactly as in the case of α-naphthaquinoline, was decomposed by warm dilute caustic soda solution, the insoluble base washed repeatedly with water, dissolved in boiling dilute hydrochloric acid, and decolorised with animal charcoal. The hydrochloride, which crystallised, was dissolved in boiling water, decomposed with ammonia, and the base thus precipitated was extracted with ether. The extract was dried with caustic soda and allowed to evaporate, when *α-acenaphthaquinoline* crystallised in colourless needles, m. p. 61—62°, which gradually turned yellow (Found : N, 7·0. $C_{15}H_{11}N$ requires N, 6·8%).

The base is insoluble in water and very soluble in ether, alcohol, or benzene. It readily forms crystalline salts with mineral acids, these being very soluble in water, less soluble in acids, and very easily decomposed by caustic alkalis. The *picrate*,

$$C_{15}H_{11}N,C_6H_2(NO_2)_3{\cdot}OH,$$

m. p. 234°, is precipitated as microscopic, yellow needles on mixing alcoholic solutions of acenaphthaquinoline and picric acid. It is insoluble in cold alcohol and difficultly soluble in boiling alcohol (Found : N, 13·1. $C_{21}H_{14}O_7N_4$ requires N, 12·9%).

α-Naphthaquinoline-6 : 7-dicarboxylic Acid (II).—An almost boiling solution of 5 g. of α-acenaphthaquinoline in 100 c.c. of glacial

acetic acid was gradually treated with 14·5 g. of powdered potassium dichromate, and the whole was boiled under reflux for about 2 hours and poured into water. The solid product, after being washed repeatedly with water, was completely extracted with hot dilute caustic soda solution, and the extract, after decolorisation with animal charcoal, was neutralised with dilute sulphuric acid. The dicarboxylic acid thus precipitated (yield 6 g.) was digested with caustic soda solution, the slightly soluble sodium salt thus formed dissolved in hot water, and the combined filtrates were boiled with charcoal. The alkaline solution was then *either* very slowly and exactly neutralised with dilute sulphuric acid—whereby the dicarboxylic acid crystallised in small, white, glistening plates—*or* made strongly acid with glacial acetic acid, whereby the dicarboxylic acid was thrown out of solution (it is not precipitated from solution by dilute acetic acid). At 150° it was completely converted into the anhydride (Found: N, 5·5, 5·8; C, 71·7; H, 2·85. $C_{15}H_7O_3N$ requires N, 5·6; C, 72·3; H, 2·8. $C_{15}H_9O_4N$ requires N, 5·2; C, 67·4; H, 3·4%).

On distillation of the acid with soda-lime, α-naphthaquinoline was obtained as a pale yellow oil which solidified immediately on inoculation. The melting point of the solid, recrystallised from light petroleum, was 49—50°, and was unchanged on admixture of α-naphthaquinoline. Its picrate, m. p. 191—192°, was identical with that of α-naphthaquinoline.

I wish to thank Mr. Holland Crompton for suggesting this work, and am continuing the investigation of the properties of the new base.

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UNIVERSITY OF LONDON. [*Received, April 6th*, 1925.]

CLXXXIII.—*The Solubility of Sulphur Dioxide in Water and in Aqueous Solutions of Potassium Chloride and Sodium Sulphate.*

By JOHN CHRISTOPHER HUDSON.

PREVIOUS experiments on the effect of neutral salts on the solubility of gases seem to have been chiefly concerned with the less soluble gases, such as hydrogen, oxygen and nitrogen, which, as a rule, cannot be estimated in solution by chemical means. In consequence the accuracy of the results is probably small compared with that obtainable for a more soluble gas, capable of estimation by chemical as distinct from physical methods. Further, most of the earlier

work on the subject deals with the relative effects of a large number of different salts under the same temperature conditions, rather than with the variation in the influence of any particular salt when these conditions are varied. It is therefore possible that the detailed study of the effect of a limited number of salts, as affected by wide variations of both temperature and concentration, may throw additional light on the factors involved. The importance of these considerations will be seen from the results given later for the solubility of sulphur dioxide in sodium sulphate solutions. In this case, the curve obtained by plotting solubility against salt concentration exhibits a maximum at certain temperatures; moreover, the effect of the salt (at certain concentrations) on the solubility changes sign with rising temperature. Hence an isolated determination at one temperature and concentration would give but an imperfect idea of the neutral salt effect.

It seemed desirable, therefore, to investigate the effect of neutral salts on the solubility of one of the more soluble gases over the widest possible ranges of temperature and concentration. Sulphur dioxide was chosen, partly for convenience and partly because the solubility of the gas in water itself had not yet been fully determined, the best results, due to Sims (J., 1862, **14**, 1), being confined to temperatures below 60°.

Although the more soluble gases, such as sulphur dioxide and ammonia, can be estimated chemically in solution with an accuracy greater than that of the absorption methods generally used for the less soluble gases, the process of solution is probably complicated in these cases by the formation of a compound between the gas and the solvent water. Indeed, it is known from the work of Fox (*Z. physikal. Chem.*, 1902, **41**, 458), Péchard (*ibid.*, 1900, **35**, 110), and others that sulphur dioxide may combine also with the added neutral salt. Thus, whereas the effect of a second solute on the solubility of the less soluble and neutral gases, where a diminution in solubility is generally observed, may be ascribed to hydration of the neutral salt, the solubility of the more soluble and reactive gases is probably determined by two main factors: compound formation, which tends to increase the solubility, and hydration of the added salt, which has the opposite effect.

The experimental work described in this paper includes a determination of the solubility of sulphur dioxide:

(1) in water between 10° and 90°,

(2) in aqueous solutions of potassium chloride, containing up to 30 g. of salt per 100 g. of water, also between 10° and 90°,

(3) in aqueous solutions of sodium sulphate, containing up to 20 g. of salt per 100 g. of water, between 20° and 50°.

The lower temperature limit (10°) is imposed by the fact that below 7° a saturated solution of sulphur dioxide is supersaturated with respect to the crystalline hydrate $SO_2,7H_2O$ (Roozeboom, *Rec. trav. chim.*, 1884, **3**, 46). On the other hand, experimental difficulties increase rapidly as the temperature rises and it was not found possible to make reasonably accurate determinations above 90°.

Experimental.

The experimental method adopted consisted in bubbling the gas through the solutions under investigation until they were saturated and then analysing them. The essential requirements of such a method include:

1. The direct measurement of the total pressure over the solution, from which the partial pressure of the gas may be calculated.

Fig. 1.

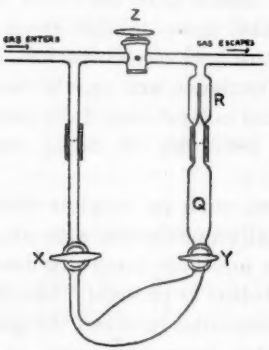
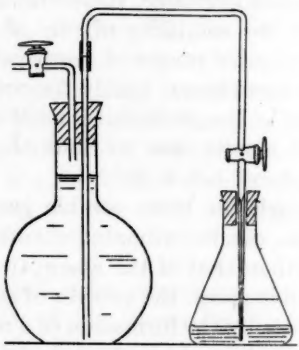


Fig. 3.



2. The complete displacement of all inert gases from the apparatus.

3. A method of sampling which does not involve a change in pressure over the solution.

4. The analysis of a sample which consists entirely of the liquid phase, so that no corrections are necessary for quantities of gas not actually dissolved.

5. An accurate method of analysis.

6. A check on the accuracy of the results by approaching the equilibrium from both sides.

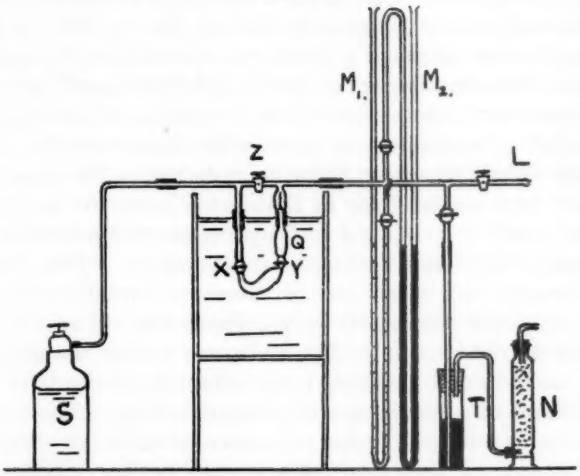
Failure to comply with one or more of these conditions has proved the weak point in previous experimental methods. For instance, a method of sampling which involves suction into a pipette cannot be expected to yield accurate results in the case of sulphur dioxide, as Lindner (*Ber. K. Akad. Wiss. Wien*, 1912, **121**, 293) remarks.

In the saturator finally adopted, the absorption bulb had a capacity of about 35 c.c. and was blown in such a form as to minimise

the head of solution through which the gas was bubbled (Fig. 1). The bulb was closed by two glass taps, X and Y. It was charged with the liquid under investigation, attached by pieces of pressure tubing to the two limbs of a double T-piece, Z, and placed in a thermostat at the required temperature. The ends of the T-piece were then connected with the gas supply and the manometers, as shown in Fig. 2.

S is a siphon of sulphur dioxide. The purity of siphon sulphur dioxide is known to be high, the chief impurity being water, which seldom exceeds 0·4%. Most of the solutions were analysed after saturation and, in these cases, the presence of water in the gas would not affect the results.

FIG. 2.



M_1 and M_2 are oil and mercury manometers respectively. The oil used was a light mineral oil of d 0·870. It absorbed sulphur dioxide, but this did not alter its density to an appreciable extent. T is a bottle containing mercury, which serves to regulate the internal pressure. N is a soda-lime tower for absorbing the excess of gas. The necessary connexions were made by small pieces of pressure tubing.

When the bulb had acquired the temperature of the bath, the apparatus was evacuated by a water-pump connected to L. Sulphur dioxide was admitted from the siphon and allowed to bubble out through T. This evacuation and sweeping out with the gas was repeated several times, so that air was completely expelled from the apparatus. When the tap Z was closed, the gas bubbled through the solution, the excess of liquid being displaced into the small bulb Q. The bubbling was continued until saturation was completed.

Half an hour was usually sufficient, but most experiments were continued for much longer periods, with a minimum of 1 hour. Tap Z was then opened; the solution flowed back into the bulb and filled it, whereupon taps X and Y were closed under water. At temperatures above 60°, owing to the running of the lubricant on the taps, it was found advisable to carry out the saturation with the taps X and Y just outside the bath. In these cases the bulb was not completely filled with solution and a small correction was therefore made for this fact.

The tube and its contents, after being disconnected and dried externally, was weighed, any solution left in Q having been removed with the help of filter-paper.

Determinations of the solubility reached from the side of supersaturation were made by passing the gas for an hour or so at a lower temperature or under a greater pressure than the equilibrium values, and then continuing the bubbling for another 3 hours at the final temperature and pressure before analysing the solution.

The analytical methods used varied with the nature of the solution.

1. *Water and Potassium Chloride Solutions.*—The sample was transferred to a conical flask as follows: About 200 c.c. of water containing some caustic soda and hydrogen peroxide were placed in the flask, which was closed by a rubber stopper. Two glass tubes passed through the latter, one of these was straight and vertical and dipped below the liquid in the flask, the other was a short piece bent at right angles. The bulb containing the sample was inverted and the end Q (Fig. 1) was attached to the long vertical tube by means of a small piece of pressure tubing. The other limb of the bulb was dipped under a further quantity of dilute alkali and hydrogen peroxide contained in a small beaker. When suction was applied through the small bent glass-tube and taps X and Y were opened, the sample was swept out into the conical flask without any loss. The total quantities of caustic soda and of hydrogen peroxide used were in slight excess of those necessary to convert the sulphurous acid completely into sodium sulphate.*

The resulting solution was heated on the steam-bath to destroy the excess of hydrogen peroxide, cooled, and diluted to 1 litre. Measured portions were then taken for the determination (in duplicate) of sulphate as barium sulphate, and of chloride as silver chloride, when necessary.

2. *Sodium Sulphate Solutions.*—As the presence of sulphate interferes with the gravimetric determinations in the case of sodium sulphate solutions, it was more convenient to estimate the dissolved sulphur dioxide volumetrically. A large number of experiments

* Analytical reagents were used.

were made on the iodimetric titration of sulphurous acid which confirmed the conclusion of Raschig (*Z. anorg. Chem.*, 1904, **17**, 577) and Macaulay (J., 1922, **121**, 553) that the low results frequently obtained in this estimation are due almost entirely to the escape of sulphur dioxide from the solutions; *e.g.*, a 0·05*N*-sulphurous acid solution, stored in a litre flask and communicating with the atmosphere only through a narrow glass tube, lost more than 1% of its strength in 40 minutes.

In order to minimise losses of sulphur dioxide, the solution obtained from the saturator was transferred to a flask of water of about 1 litre capacity so that it filled the latter almost completely. The flask, containing the diluted sulphurous acid solution, was weighed and was then fitted with a siphon ending in a glass tap and capillary jet (Fig. 3). The iodine solution was stored in a large stock bottle of the type recommended by Rice, Kilpatrick, and Lemkin (*J. Amer. Chem. Soc.*, 1923, **45**, 1361), which was also fitted with a glass tap and capillary jet. About 70 c.c. of water were introduced into a small conical flask, followed by about 30 g. of iodine solution, the flask and contents being weighed before and after the introduction of the iodine. The weight of solution removed on the tip of the capillary tube was found to be negligible. When the iodine was run in slowly, it formed a distinct layer under the water so that loss of iodine was reduced considerably. The sulphurous acid was then run in until the colour of the iodine was discharged and a third weighing gave the weight of sulphurous acid. The final end-point was obtained by the addition of starch and small quantities of a very dilute iodine solution until the solution assumed a standard tint.

Three titrations were made and approximately 80 c.c. of the sulphurous acid were used altogether, so that the volume of the gaseous phase over the solution of sulphur dioxide in the flask seldom exceeded 150 c.c. and was often less. Consequently, the maximum loss arising from evaporation of the sulphur dioxide into the gaseous space above the solution, on the assumption that all the gas was originally in the solution, that no diffusion occurs into the atmosphere, and that there is no oxidation,* should not exceed 0·4%.

The following results for a given sulphurous acid solution serve to show the accuracy which may be obtained by this method:

Wt. of iodine soln. (g.)	19·705	22·085	19·755
Wt. of sulphurous acid soln. (g.)	26·495	29·71	26·60
Ratio	0·7437	0·7434	0·7427

* Atmospheric oxidation of dilute sulphurous acid solutions is almost negligible over short periods. Thus experiments showed that several hours elapsed before such solutions, exposed to the air in test-tubes, gave any turbidity with barium chloride in dilute hydrochloric acid.

The iodine solutions employed were standardised against anhydrous sodium thiosulphate (see Young, *J. Amer. Chem. Soc.*, 1904, **26**, 1028).

The procedure for the titration of iodine by sulphurous acid described above was found to double the accuracy of the method. The maximum difference between any two titrations of the same solution amounted to 0·43% (mean from 26 series) as against 0·88% for the ordinary volumetric method (12 series). Further, the new method gave results in good agreement with the gravimetric values. It was found, again in agreement with Macaulay, that, if rigorous precautions are taken to prevent volatilisation, it is immaterial whether the sulphurous acid solution is added to the iodine (A) or *vice versa* (B); the iodine solution was *ca.* 0·09(weight)N:

Ratio I_2/SO_2 *by Weight.*

A	0·7071	0·7050	0·7062	Mean 0·7061
B	0·7070	0·7043	0·7048	Mean 0·7054

The solutions of sodium sulphate were prepared directly by weight from the analytically pure salt. Concentration changes due to evaporation of the water whilst the gas was bubbling through the solution were minimised by previously passing the gas through a solution of approximately the same composition as that being saturated. As a check, the tubes and contents were weighed before and after saturation. The observed increase in weight was usually equal to the amount of sulphur dioxide found by analysis.

Temperature	20°	30°	40°	50°	50°	60°
Increase in weight...	3·31	2·52	1·80	1·51	1·64	1·23 g.
SO_2 found	3·28	2·55	1·84	1·52	1·64	1·40 „
Difference	0·03	0·03	0·04	0·01	—	0·17 „

As the weight of water in the sample was about 30 g. and the sulphur dioxide was actually estimated in the solutions, these small differences, which affect the water only, are within the limits of experimental error between 20° and 50°. Above 50°, the loss of water by evaporation is much greater and there is correspondingly less certainty that the final concentration of the salt is equal to its initial value.

Calculation of Results.—In order to illustrate the method of calculation, a typical experiment will be described in detail.

The lowering of the vapour pressure of water by both the dissolved gas and the added neutral salt has been assumed equal to the sum of the depressions which would have been caused by each solute separately. The lowering of the vapour pressure due to the sulphur dioxide was calculated by Raoult's law on the assumption that water is bimolecular. The correction is not great, ranging

from 0·1% at 10° to 1·25% at 90°. These figures are probably less than the experimental errors at these temperatures.* On the other hand, the correction for dissolved salt is considerable, rising in the case of potassium chloride to approximately 75 mm. at 90° for a solution containing 30 g. of salt per 100 g. of water. The values were calculated from Tammann's data (*Wied. Ann.*, 1885, **24**, 530).

The foregoing corrections are only approximate, as there are grounds for believing that sulphur dioxide combines both with the water and with the added salts, and, therefore, neither Raoult's law nor the empirical formula deduced from Tammann's data can be regarded as strictly applicable. Nevertheless, some such correction is essential and the mode of attack adopted seems the only one available at present. In order that others may be able to correlate their results with the present values, the total pressure actually measured over the solution is given for the experiments in water and potassium chloride solutions without any correction other than that for the temperature of the barometer.

Experiment 99. At 90°.

Internal volume of the bulb as determined by calibration with water, 42.8 c.c.

Sample: wt. 38·46 g.; *d* 1·17. Therefore volume, 32·9 c.c.

Vol. of gas, 42·8—32·9 = 9·9 c.c.

Wt. of $BaSO_4$, 0·3909, 0·3902 g. (250 c.c. for analysis.) Therefore total SO_2, 0·4287 g.

Wt. of AgCl, 0·8690, 0·8697 (49·92 c.c. for analysis). Therefore wt. of KCl, 9·385 g.

Wt. of water in the sample = 38·46 − 0·429 − 9·385 = 28·65 g.

G. of KCl per 100 g. of water = 9·385 ÷ 0·2865 = 32·75.

Barometer, 764·0 mm. Mercury manometer, 205 mm. Temperature correction, 3·4 mm.

Vapour pressure of water at 90°, 525·9 mm.

Calc. lowering of the vapour pressure: (*a*) By SO_2, 5·2 mm.; (*b*) By KCl, 75·5 mm. Therefore corrected vapour pressure, 525·9 − 5·2 − 75·5 = 445·2 mm.

Partial pressure of the sulphur dioxide over the solution, 764·0 + 205 − 3·4 − 445·2 = 520 mm.

Wt. of 9·9 c.c. of SO_2 at 90° and 520 mm., 0·0145 g.† Therefore SO_2 dissolved, 0·4287 − 0·0145 = 0·4142 g.

* Even if Kendall's contention (*J. Amer. Chem. Soc.*, 1921, **42**, 1391) that, in such calculations, the molecular weight of water should be taken as 18, is accepted, the differences involved have no significance in the present case.

† The weight of water vapour contained in the gaseous space is negligible.

Solubility, assuming Henry's law, $\frac{0{\cdot}4142 \times 760 \times 100}{520 \times 28{\cdot}65} = 2{\cdot}113$ g. of SO_2 per 100 g. of water, containing 32·75 g. of potassium chloride.

The experimental results are recorded in the following tables and figures: P = total pressure. p = partial pressure of sulphur dioxide. S_1 = g. of sulphur dioxide per 100 g. of water. y = g. of potassium chloride per 100 g. of water. z = g. of sodium sulphate per 100 g. of water. The solubility (S_0 or S) = $S_1 \times 760/p$, the weight of sulphur dioxide dissolved per 100 g. of water, the partial pressure of the gas over the solution being 760 mm. of mercury.

TABLE I.

The Solubility of Sulphur Dioxide in Water (See also Fig. 4).

P.	p.	S_1.	S_0.	P.	p.	S_1.	S_0.
Temp. 10°.				Temp. 48·15°.			
777·3	764·2	15·53	15·44	799·0	717·0	4·147	4·395*
776·3	767·1	15·50	15·36	801·5	719·5	4·132	4·365
776·2	767·0	15·58	15·44	794·3	712·3	4·108	4·382
775·4	766·2	15·48	15·36	840·9	758·9	4·409	4·415
766·2	757·0	15·28	15·32*			Mean	4·39
		Mean	15·39				
Temp. 15°.				Temp. 60°.			
769·5	757·6	12·72	12·76	881·5	735	3·151	3·257
772·5	760·6	12·75	12·74	894·5	748	3·192	3·244
769·5	757·6	12·64	12·68	894·5	748	3·215	3·268
		Mean	12·73	886·5	740	3·142	3·220*
						Mean	3·25
Temp. 20°.				Temp. 70°.			
787·7	771·3	10·79	10·63	897	666·5	2·278	2·598
773·3	765·9	10·61	10·66	892·5	662	2·277	2·614
778·6	762·2	10·68	10·64	893	662·5	2·300	2·637*
779·1	762·7	10·65	10·61	892	661·5	2·251	2·585*
773·9	757·5	10·64	10·68*			Mean	2·61
		Mean	10·64				
Temp. 29·9°.				Temp. 80°.			
798·5	768·5	7·640	7·554*	883	531·5	1·496	2·139
789·4	759·4	7·600	7·607	883	531·5	1·490	2·131
791·0	761·0	7·610	7·600*	958	606·5	1·704	2·130*
800·9	770·9	7·674	7·565	967	616	1·714	2·114*
		Mean	7·58			Mean	2·13
Temp. 40°.				Temp. 90°.			
800·9	747·3	5·428	5·520	893	378	0·901	1·801
801·4	747·8	5·441	5·529*	954·3	439·5	1·037	1·785
798·1	744·5	5·406	5·516	960	439	1·056	1·829
816·7	763·1	5·593	5·569			Mean	1·805
815·7	762·1	5·585	5·555*				
815·7	762·1	5·581	5·550*				
		Mean	5·54				

* denotes a supersaturation experiment.

TABLE II.

The Solubility of Sulphur Dioxide in Potassium Chloride Solutions

(See also Fig. 5).

P.	*p.*	*y.*	S_1.	*S.*	*P.*	*p.*	*y.*	S_1.	*S.*
Temp. 10°.					Temp. 48·15°.				
		0		15·39			0		4·39
780·3	772·0	5·55	17·32	17·05	841·8	761·7	5·06	4·712	4·70
780·3	772·2	10·22	18·88	18·58	841·8	763·6	10·14	4·968	4·945
766·2	758·3	15·85	20·23	20·28*	826·9	750·7	15·82	5·180	5·24
766·2	758·4	20·78	21·92	21·96*	839·8	765·7	21·11	5·521	5·48
768·2	761·4	29·90	25·45	25·40	826·9	754·0	25·09	5·703	5·74
					839·8	769·7	32·72	6·258	6·18
Temp. 15°.					Temp. 60°.				
		0		12·66			0		3·25
772·2	760·8	10·39	15·30	15·32	889	746	5·30	3·384	3·45
771·9	761·0	19·91	17·67	17·64	888	748	10·67	3·468	3·52
772·2	761·9	30·71	20·64	20·59	896	763·5	21·12	3·943	3·92
					890·5	764	30·98	4·258	4·24
Temp. 20°.					Temp. 70°.				
		0		10·64			0		2·61
773·9	757·9	5·14	11·60	11·62*	969	747·5	8·74	2·756	2·80
774·6	758·9	10·30	12·50	12·52	960·5	752	21·68	3·016	3·05
778·0	761·7	15·61	13·58	13·55	960	757	30·73	3·251	3·26
774·0	759·4	24·98	15·37	15·38					
779·0	764·8	30·38	16·76	16·65*					
Temp. 29·9°.					Temp. 80°.				
		0		7·58			0		2·13
788·6	759·3	5·19	8·204	8·21	958	620	8·66	1·850	2·27
789·4	760·7	10·11	8·810	8·80	961	643	21·35	2·043	2·415
784·0	756·7	20·82	10·00	10·05	961	656	29·68	2·179	2·52
782·8	756·8	29·86	11·21	11·26					
Temp. 40°.					Temp. 90°.				
		0		5·54			0		1·81
816·7	764·3	5·17	5·994	5·96	967·5	468	9·23	1·142	1·855
818·1	766·9	10·20	6·380	6·32	958	482	19·49	1·248	1·97
810·4	759·2	10·40	6·380	6·39*	965·5	520	32·75	1·445	2·11
818·1	768·1	15·44	6·869	6·675					
810·4	761·6	20·14	7·086	7·07*					
803·7	756·0	24·83	7·415	7·45					
803·7	757·0	28·95	7·721	7·75					

* denotes a supersaturation experiment.

TABLE III.

The Solubility of Sulphur Dioxide in Sodium Sulphate Solutions

(See also Fig. 6).

Temp. 20°							
z	0	1·94	4·93	7·95	10·00	15·00	20·00
S_1	10·64	10·66	10·57	10·36	10·07	9·66	9·17
Temp. 30°							
z	0	2·04	3·99	5·47	7·83	10·00	20·01
S_1	7·608	7·709	7·776	7·773	7·716	7·586	7·006
Temp. 40°							
z	0	2·49	5·04	7·95	10·00	14·94	20·01
S_1	5·585	5·812	5·910	5·927	5·882	5·802	5·630
Temp. 50°							
z	0	2·49	5·04	10·04	14·94	19·99	
S_1	4·214	4·508	4·678	4·728	4·730	4·648	

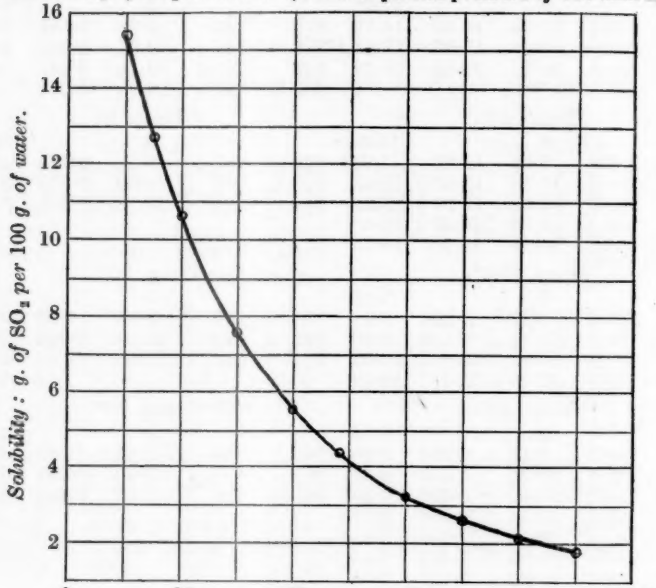
Details of the total and partial pressures have been omitted in Table III because, except in three cases, the calculated value of the partial pressure of the gas over the solution was within 10 mm. of 760 mm. The results were corrected to 760 mm. on the basis of Henry's law.

Discussion of Results.

A. Solubility in Water.—The solubility of sulphur dioxide in water was first determined by Schönfeld (*Annalen*, 1855, **95**, 1).

FIG. 4.

The solubility of SO_2 *in water.* (*Under a partial pressure of* 760 *mm. Hg*).



The results obtained—quoted to five significant figures—are the only ones given in the most recent edition of Landolt and Börnstein's Tables.

Apart from grave sources of error in this work, such as failure to correct for the vapour pressure of water, erroneous values for the densities of the solutions (see Roozeboom, *Rec. trav. chim.*, 1884, **3**, 57), and the doubtful accuracy of the method of analysis, it should be noted that the solubilities given in Landolt and Börnstein's Tables are calculated from two quadratic formulæ deduced by Schönfeld. Since, however, the percentage differences between the calculated and the observed values for Schönfeld's nine experi-

mental points are $-1{\cdot}1$, $+2{\cdot}7$, $-0{\cdot}6$, $-2{\cdot}2$, $+4{\cdot}0$, $-1{\cdot}0$, $-2{\cdot}5$, $+5{\cdot}5$, $-2{\cdot}1$, it appears that the five significant figures given in the Tables have little meaning.

It is surprising that the results obtained by Sims (J., 1862, **14**, 1) should have been overlooked. The results obtained in the present investigation agree well with his values, although somewhat lower figures are obtained at the higher temperatures in agreement with Smith and Parkhurst (*J. Amer. Chem. Soc.*, 1922, **44**, 1918), who state that their results are consistently below those of Sims. These American investigators were chiefly concerned with the solubility of sulphur dioxide in suspensions of calcium and magnesium hydroxides, and the number of actual experimental determinations of the solubility in water itself reported in their paper is small. Their values for the solubility are recorded in the comparative table below. The agreement is good, save at 60°, but it should be noted that the solubility value at this temperature quoted for Smith and Parkhurst is based on the figure obtained with a partial pressure of sulphur dioxide of only 175·7 mm. The necessary extrapolation, based on Henry's law, to the standard pressure of 760 mm. gives a value 3·63 as against 3·25 obtained in the present investigation, but, as shown by Sims and Lindner, this extrapolation will undoubtedly give too high values of the solubility. Lindner (*Ber. K. Akad. Wiss. Wien*, 1912, **121**, 293) explained the deviations from Henry's law on the hypothesis that the ratio of the concentrations of the free sulphur dioxide molecules, as distinct from the ionised sulphurous acid, was constant for the two phases and, using Sim's data, he obtained results in good quantitative agreement with this suggestion. He was less fortunate, however, with results which he obtained himself. He made only four experiments; the value quoted below for 50° is extrapolated from a measurement at 700 mm. In his other experiments, the partial pressure of the gas was small compared with one atmosphere, so that accurate extrapolation is not possible.

In the present series of experiments, errors due to deviation from Henry's law were reduced to a minimum at all temperatures up to 60° by arranging that the partial pressure of the gas should be as nearly atmospheric as possible. This was done by adjusting the height of the mercury in the bottle T (Fig. 2). Owing to the rapid rise in the vapour pressure of water, it was not possible to do this at higher temperatures, since the glass taps would not withstand considerable internal pressures. On the other hand, there is less objection to the application of Henry's law at higher temperatures.

A comparative table of the results of various investigations is given below.

Solubility of Sulphur Dioxide in Water.

	Schönfeld.	Sims.	Smith and Parkhurst.	Lindner.	Hudson.
10°	16·21	15·4			15·39
15	13·54	12·55			12·73
20	11·28	10·4	10·81		10·64
25	9·41	8·95			8·98
30	7·80	7·8			7·56
40	5·41	5·8	5·52		5·54
50		4·5		3·95	4·14
60			3·63		3·25

The values for the solubility given above are expressed as g. of sulphur dioxide per 100 g. of water when the partial pressure of the gas is 760 mm. of mercury, with the following exceptions:

1. Schönfeld's results refer to a *total* pressure of 760 mm.
2. Smith and Parkhurst, and Lindner gave their results in terms of 100 *c.c.* of water.

B. Solubility in Salt Solutions.—It will be seen from Fig. 5, in which the solubility of sulphur dioxide is plotted against the concentration of potassium chloride, that the curves obtained are very nearly straight lines at all temperatures, in agreement with the results of Fox (*loc. cit.*) for this salt at 25° and 35°. If S is the solubility of the gas in a solution containing y grams of potassium chloride per 100 grams of water, then the formula $S = S_0 + ay$ represents the results with considerable accuracy. The most probable values of the constants S_0 and a (calculated by the method of mean squares) are given in the following table, together with the corresponding values of the relative increase in solubility, which may conveniently be taken as the percentage increase in the solubility per gram of salt added, and which is given by

$$k = \frac{S - S_0}{S_0} \cdot \frac{100}{y} = \frac{100a}{S_0}.$$

Temp.	S_0.	a.	k.	Temp.	S_0.	a.	k.
10°	15·21	0·3328	2·187	48·15°	4·399	0·05352	1·217
15	12·66	0·2534	2·017	60	3·267	0·03007	0·920
20	10·57	0·1958	1·852	70	2·615	0·02059	0·787
29·9	7·567	0·1223	1·616	80	2·142	0·01294	0·604
40	5·557	0·07565	1·361	90	1·793	0·00939	0·524

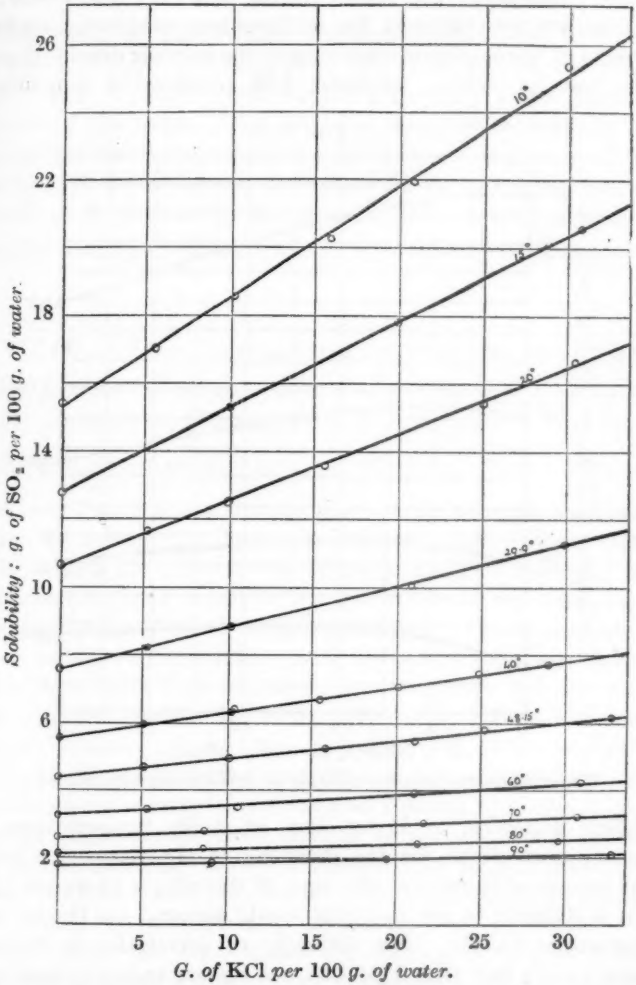
The values of S_0 obtained in this way are generally in good agreement with the experimental values for the solubility of sulphur dioxide in water, as tabulated on page 1340. At 10° and 15°, however, the differences between the observed and the calculated values of S_0 are somewhat greater, corresponding probably with a slight departure from the linear relationship at these temperatures.

The results for the solubility of sulphur dioxide in sodium sulphate

solutions are rather surprising. At 30°, 40°, and 50°, the solubility-salt concentration curves exhibit distinct maxima, as shown in Fig. 6. There is probably a maximum solubility at 20° also.

FIG. 5.

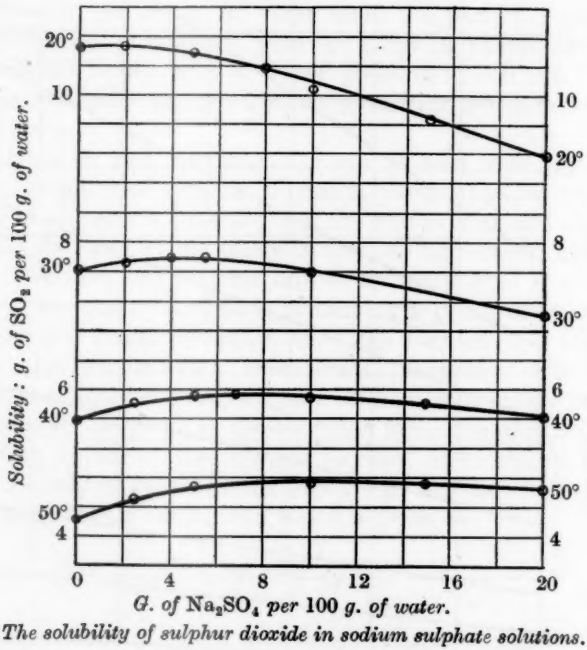
The solubility of sulphur dioxide in aqueous solutions of potassium chloride.



The actual position of the maximum is difficult to determine, but it is clear that it moves to the left with falling temperature. A few experiments at 10°, not reported here, render it possible that the maximum may disappear altogether at this temperature, but further experimental evidence is necessary to establish this point.

Fox (*loc. cit.*) investigated the solubility of sulphur dioxide in a large number of salt solutions at 25° and 35°. It is rather difficult to correlate his results with the present values, as he expressed them in terms of the solubility coefficient, and, in order to effect a comparison, a knowledge of the densities of the various solutions would be necessary. The values for the densities of solutions of the salts alone are not sufficient, for, at these temperatures, considerable expansion of the solutions occurs when the sulphur dioxide dissolves. In the case of sodium sulphate, Fox observed a diminution in

FIG. 6.



The solubility of sulphur dioxide in sodium sulphate solutions.

solubility following a linear law at both temperatures. The necessary corrections for the densities of the respective solutions might conceivably reverse the sign of the effects observed by him, but it is difficult to see how this would account for the occurrence of maximum values. The difficulty of correlation is further increased by the fact that Fox does not appear to have measured the pressures over his solutions.

As suggested on page 1334, the two main factors determining the solubility of sulphur dioxide in salt solutions are probably the hydration of the salt and the tendency to combination between the salt and the gas. It might be possible, on the basis of the hydration

values for salts already on record, to attempt an estimate of the significance of these two factors, but it is felt that such an attempt should be postponed until a much larger mass of experimental data for the influence of neutral salts on the solubility of this gas over a wide temperature range is available.

In conclusion, the author desires to express his thanks to Professor J. C. Philip, F.R.S., who suggested this research, for the valuable assistance and criticism which he has generously given throughout the course of the work. The author is indebted also to Dr. H. F. Harwood for advice concerning the methods of analysis, and to the Department of Scientific and Industrial Research for a grant which has rendered it possible for him to undertake this investigation.

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CLXXXIV.—*Low Temperature Oxidation at Charcoal Surfaces. Part I. The Behaviour of Charcoal in the absence of Promoters.*

By ERIC KEIGHTLEY RIDEAL and WINIFRED MARY WRIGHT.

THE results of numerous investigations on the adsorption of oxygen by charcoal, notably by Baker (J., 1889, **51**, 249), Dewar (*Compt. rend.*, 1904, **139**, 201), Rhead and Wheeler (J., 1913, **103**, 461, 1210), and Hulett (*J. Amer. Chem. Soc.*, 1920, **42**, 1408), indicate that oxygen may be adsorbed on a charcoal surface to form at least three types of surface compounds*; one removable only as oxides of carbon at extremely high temperatures (*ca.* 1000°), another removable as oxides of carbon by evacuation or by fusion with sodium carbonate (Taylor, *J. Amer. Chem. Soc.*, 1921, **43**, 2059), and a third, formed in larger quantities by adsorption at low temperatures, which can be recovered as oxygen (Dewar and Hulett).

The last form of adsorbed oxygen is endowed with catalytic properties, for not only does low-temperature autoxidation of the charcoal with liberation of carbon dioxide occur, but many oxidative processes may be catalytically accelerated by charcoal. Thus, Calvert (J., 1867, **20**, 293) noted the oxidation of ethyl alcohol vapour and gaseous hydrocarbons, recently confirmed by Firth (*Trans. Faraday Soc.*, 1924, **20**, 370). Feigel (*Z. anorg. Chem.*, 1921, **119**, 305) noted the catalytic oxidation of solutions of sulphides,

* Professor Armstrong has pointed out that there exist three forms of carbon in charcoal, *viz.*, diamond, paraffin, and ethenoid (to which the colour is due).

chromates and iodides. The investigations of Warburg and his co-workers on the catalytic oxidation of oxalic acid and certain α-amino-acids (*Pflüg. Arch.*, 1914, **155**, 547; *Biochem. Z.*, 1921, **113**, 257), of Meyerhof on the oxidation of glucose in the presence of phosphoric acid (*Biochem. Z.*, 1923, **135**, 558) are the most complete in this respect.

Warburg (*ibid.*, 1924, **145**, 461) has shown that the property of charcoals of adsorbing solutes from aqueous solution is not connected with their catalytic powers, and suggested, somewhat vaguely, a differentiation of the charcoal surface into two modifications, both of which adsorb solutes but only one is catalytically active. He showed that sugar charcoal does not owe its catalytic properties to iron, although iron in certain forms is a very definite promoter. The results of the determinations of the velocity coefficients of the reactions by Freundlich, Warburg, and Negelein may be summarised as follows :—

(1) The reaction velocity varies inversely as the concentration of the solute, in the case of oxalic acid.

(2) The reaction velocity varies as the square root of the oxygen pressure, in the case of phenylthiocarbamide.

(3) The temperature coefficients for the oxidation of oxalic acid and cystine on blood charcoal are 2·1 and 2·3 respectively.

Freundlich and Bjerke (*Z. physikal. Chem.*, 1916, **91**, 31) considered that the mechanism of the oxidation of phenylthiocarbamide consisted in the adsorption of a film of the substance on the surface of charcoal, the film thickness varying as the bulk concentration of the solute. The oxygen had to diffuse through this film for reaction, and the diffusion rate was assumed to vary as the square root of the gas pressure.

The experimental results of Warburg for cystine, however, do not agree well with the square-root relationship of Freundlich for phenylthiocarbamide. Langmuir (*J. Amer. Chem. Soc.*, 1918, **40**, 1361), in discussing his theory of the unimolecular nature of the adsorbed film, suggested that the oxygen molecule on striking a charcoal surface would occupy two elementary spaces on the lattice, and that the oxygen atom on each space would take part in the reaction; the concentration of oxygen atoms on the surface could then be regarded as proportional to the square root of the oxygen pressure.

That a difference in properties of various parts of a clean catalyst-surface must exist, has long been known, and can readily be deduced from a consideration of the various physical modifications of the material which exist on the surface, *e.g.*, crystal facets, edges, and partly isolated atoms, each form possessing different surface energy. From the effect of minute traces of poisons on the catalytic activity,

also, although less conclusively, from the variation in the magnitudes of the saturation maximum of adsorption of various gases, similar conclusions as to the existence of areas of different activity on a surface may be drawn. The first quantitative attempt to determine the area of the catalytically active portion of a solid catalyst was made by one of us (Rideal, J., 1922, **121**, 309) in an examination of the catalytic efficiency of a nickel surface for the combination of ethylene and hydrogen. The work of Pease (*J. Amer. Chem. Soc.*, 1923, **45**, 1196) on quantitative poisoning provides data for similar calculations on a copper surface; whilst in solutions the question of fractional poisoning has been investigated by Maxted (J., 1922, **121**, 1760) and by Vavon and Husson (*Compt. rend.*, 1922, **175**, 277). In the case of charcoal, it is to be anticipated, on this conception of a variability of surface activity, that the existence of different forms of surface should be capable of experimental demonstration. A number of carbon atoms in the surface may be regarded as being readily detachable, being held less tenaciously than atoms in the regular space lattice, and should readily react with oxygen and be disengaged as carbon dioxide, and constitute the autoxidisable fraction. There exists in addition a fraction of the surface on which oxygen is strongly adsorbed, but from which carbon dioxide can be evolved only at high temperatures; this composite surface is very stable, and adsorbed molecules on it either evaporate unchanged or remain as a compound on the surface, no catalytic action taking place. Thus diamond facets adsorb dyes with facility, but do not promote catalytic oxidation. In addition to these two extremes, there exists a portion of the surface from which carbon dioxide may be evolved at comparatively low temperatures; this oxygen complex apparently passes over to the more stable form with time. The union of the carbon atoms with the underlying solid is in this case less strong than in the former but stronger than for the autoxidisable surface, and the adsorbed reactant oxygen on excitation is capable either of entering into a more complete combination with the underlying carbon or of oxidising a molecule of an oxidisable reactant adsorbed in juxtaposition to it.

The data on the heat of adsorption of oxygen by charcoal (Blench and Garner, J., 1924, **125**, 1288) provide additional support for such an assumption, for they found that the heat of adsorption is in part greater than the heat of oxidation of carbon. Since the energy of oxidation of carbon involves the endothermic breaking of carbon linkings, Garner's data indicate that on the surface of carbon some of the linkings in the carbon skeleton are already broken. These atoms are less saturated than those completing a graphite ring, and we should anticipate that they would possess a greater chemical

reactivity. An attempt has now been made to measure the areas of these different surfaces on the charcoal, and the effects of variation in oxygen pressure and in concentration of acid on the rate of oxidation on the surface have been investigated.

Experimental.

A. Autoxidation.

Kahlbaum's sugar charcoal was washed in silica vessels with boiling conductivity water to remove soluble impurities and dried by heating in a platinum dish; one portion was activated by heating in silica vessels by Millar's method (*J. Amer. Chem. Soc.*, 1922, **44**, 1866), another by heating in a stream of hydrogen. The resulting charcoals were equally active, and retained their activity when preserved from contamination, or exposure to the laboratory air.

The charcoal contained 1·1% of ash, chiefly silica, calcium, potash, and a trace of iron (0·8% of the ash). The mean diameter of the charcoal particles was 0·4μ (average of 200 counts).

The rate of autoxidation of this charcoal was determined by measuring the rate of oxygen uptake, from air and from oxygen, and of evolution of carbon dioxide, from 100 mg. of charcoal suspended in 3 c.c of conductivity water in a shaking apparatus with a Barcroft differential manometer (*Biochem. Z.*, 1917, **81**, 319). In one set of experiments, the carbon dioxide was absorbed in a 40% solution of potash, so that the pressure change was proportional to the oxygen-uptake. In another series, no potash was used, so that the pressure change was proportional to the difference in the amounts of the carbon dioxide evolved and the oxygen taken up. There is a small error due to the carbon dioxide adsorbed by the charcoal and that dissolved in the water, but after about 4 hours the amount adsorbed is negligible compared with that evolved.

The reaction velocity after preliminary agitation of the mixture for ½ hour conformed to a reaction of zero order, and for every molecule of oxygen adsorbed an equivalent of carbon dioxide was evolved.

The oxygen uptake is given in the following table, also the velocity coefficient k, calculated in cubic mm. of oxygen per hour (N.T.P.) per mg. of charcoal.

From these data the temperature coefficient is found to be $k_{50°}/k_{40°} = 1·8$. Also the rate of autoxidation is independent of the oxygen pressure over the range of pressures examined.

As has been indicated, we should anticipate autoxidation to occur only on highly active patches on the carbon surface. These are always saturated with adsorbed oxygen, and the rate of reaction

Time (hrs.).	Partial pressure of $O_2(P)$ 754 mm. Temperature (t) 40°.	$P = 176{\cdot}2$. $t = 40°$.	$P = 176{\cdot}2$. $t = 50°$.
1	2·3	2·0	3·5
1½	3·0	2·8	4·9
2	4·0	3·5	6·2
2½	4·3	4·2	7·6
3	5·4	4·9	9·0
3½	6·4	5·7	10·3
4	7·0	6·5	11·6
4½	7·8	7·3	12·9
5	8·4	8·0	14·3
5½	9·0	8·9	15·7
6	10·6	9·5	17·0
	$k = 0{\cdot}013$	$k = 0{\cdot}013$	$k = 0{\cdot}023$

measured is the rate of evaporation of carbon dioxide from them, a reaction of zero order (compare Langmuir, *J. Amer. Chem. Soc.*, 1916, **40**, 1361).

If we imagine the surface combustion as spreading out superficially as a ring, the rate of autoxidation should increase as the circumference of the ring increases; the reaction would thus be autocatalytic in behaviour. On the other hand, if it be imagined that combustion proceeds along a chain of carbon atoms, the zero order of such a combustion process is readily intelligible.

Substances strongly adsorbed by charcoal will be preferentially adsorbed on the most active areas of the charcoal surface, and since the rate of evaporation will be slow from such surfaces, it is possible to poison such areas preferentially. As poisons, potassium ferricyanide and amyl alcohol were employed. The adsorption isotherms were determined, the former colorimetrically and the latter by surface-tension measurements. The amounts of poison adsorbed by 100 mg. of charcoal necessary completely to arrest autoxidation are given in the following table:

Poison.	G.-mol. adsorbed by 100 mg. of charcoal.	No. of autoxidisable atoms per mg. of charcoal.
Potassium ferricyanide	$3{\cdot}6 \times 10^{-7}$	$3{\cdot}6 \times 10^{-9} \times 6{\cdot}06 \times 10^{23} = 2{\cdot}38 \times 10^{15}$
Amyl alcohol	$9{\cdot}0 \times 10^{-7}$	$9 \times 10^{-9} \times 6{\cdot}06 \times 10^{23} = 5{\cdot}45 \times 10^{15}$

The ferricyanide method probably gives the more accurate value, not only on account of the greater sensitivity of the colorimetric method for small concentrations, but also on account of the stronger adsorptive power of the charcoal for the ion rendering the action of poisoning more selective. Some uncertainty is introduced by the assumption that the ferricyanide ion occupies but one elementary atom on the carbon surface; since, however, the autoxidisable area is relatively small, the probability of two autoxidisable atoms being in contact with each other is remote.

The total area per mg. of charcoal was determined from the surface saturation value of amyl alcohol. For saturation, the fraction

of a gram-molecule of amyl alcohol adsorbed per mg. of charcoal was found to be $1{\cdot}04 \times 10^{-6}$, hence the number of atoms on the surface of one mg. is $6{\cdot}30 \times 10^{17}$; since the density of charcoal is 2·16, the surface per mg. of charcoal is 0·0266 square metre,* a value in good agreement with that given by Paneth and Radu (*Ber.*, 1924, **57**, 1221), who obtained for similar charcoal an area of 0·0248 sq. metre per mg.

From the areas given by adsorption measurements the fraction of the surface autoxidisable is $2{\cdot}38 \times 10^{15}/6{\cdot}3 \times 10^{17} = 0{\cdot}38\%$. The rate of autoxidation at 40° is 0·013 c.mm. of oxygen per mg. of charcoal per hour, equivalent to a carbon consumption of $3{\cdot}51 \times 10^{14}$ atoms per hour. Thus, the average life of one of the autoxidisable carbon atoms on the surface is $2{\cdot}38 \times 10^{15}/3{\cdot}51 \times 10^{14}$ or 7 hours. The mechanism of the autoxidation process may probably be represented most conveniently by the following equations:

$$C + 2H_2O + O_2 \longrightarrow C\begin{matrix}OH{-}H\ldots O\\ OH{-}H\ldots O\end{matrix} \longrightarrow CO_2 + \begin{matrix}H_2O\\ H_2O\end{matrix}$$

B. *The Catalytic Oxidation of Organic Acids.*

A consideration of the published data on the oxidation of oxalic acid and various α-amino-acids indicates that the conclusions already summarised (p. 1348) cannot be regarded as correct, although these relationships do obtain over a somewhat limited range of concentration.

The investigations of Langmuir make it probable that the oxygen molecule in the reactive state actually occupies two elementary spaces on the space lattice, thus justifying the square-root relationship obtained. There is little doubt that the substance undergoing oxidation is likewise adsorbed, but that the velocity of oxidation should be inversely proportional to its bulk concentration for extremely dilute solutions is improbable.

It is to be anticipated that, as in the combination of ethylene and hydrogen at nickel and copper surfaces (J., 1922, **121**, 309) or the oxidation of sulphur dioxide at a platinum surface, the reaction velocity should be proportional to the surface concentrations of both reactants, and should thus attain to a maximum when the surface phase consists of an optimum mixture for reaction to occur, the velocity sinking on each side as one or other reactant is increased in quantity.

We have found that in aqueous solutions substances containing

* This calculation may also be performed in the following manner: Since the area of a benzene ring is 25Å (the maximum area parallel to the cleavage plane in graphite), the area for each atom is 25/6Å, thus the area of $6{\cdot}30 \times 10^{17}$ atoms is 262 sq. cm. or 0·0262 sq. metre.

but one polar group, such as alcohol, formic, acetic, and the higher fatty acids, do not undergo oxidation at the surface of charcoal. On the other hand, substances containing two adjacent polar groups, one of which may be a mobile hydrogen atom, such as α-amino-acids, phenylthiocarbamide, oxalic and malonic acids, are readily oxidised, a similar phenomenon to that noted by Kruyt and van Duin (*Proc. K. Akad. Wetensch. Amsterdam*, 1923, **25**, 234) in their investigations on the acceleration of the removal of bromine from ββ-dibromopropionic acid in the presence of charcoal; whilst α-amino-acids undergo oxidation, monochloroacetic acid is not oxidised.

In confirmation of Warburg's work on the oxidation of oxalic acid the ratio of carbon dioxide evolved to oxygen adsorbed was found to be 4 : 1, agreeing with the equation $2H_2C_2O_4 + O_2 = 4CO_2 + 2H_2O$. The temperature coefficient was $k_{50°}/k_{40°} = 2{\cdot}0$, compared with Warburg's value of 2·1 for iron-containing charcoal. Malonic acid also was oxidised, the ratio found, $CO_2/O_2 = 1 : 1$, agreeing with the equation

$$2CH_2(CO_2H)_2 + O_2 \longrightarrow 2CH(OH)(CO_2H)_2 \xrightarrow{O_2} 2CHO{\cdot}CO_2H + 2CO_2 + 2H_2O.$$

Glyoxylic acid was identified by the indole–sulphuric acid reaction. The reaction velocities of acid oxidation were much greater than the autoxidative process, although the temperature coefficients from which energies of activation are frequently calculated are likewise higher (1·8 : 2·0). This is an indication that the oxidation is proceeding on another portion of the charcoal, greater in extent than that undergoing autoxidation. This view was confirmed by showing that the two reactions, the autoxidation and the acid oxidation, were not coupled reactions * and that the autoxidisable areas could be poisoned selectively without interfering with the process of catalytic oxidation.

The influence of variation in the concentration of oxalic acid at constant oxygen pressures as well as the effect of an increase in oxygen pressure is shown in the curves in Figs. 1 and 2.

As was anticipated, the velocity rises to a well-defined maximum with increasing acid concentration, subsequently falling off as the

* It is frequently assumed that *all* such reactions are coupled, involving the intermediate formation of hydrogen peroxide. On this hypothesis the above reaction could be written :

$$C + 2H_2O \rightarrow C\begin{matrix}OH{\cdot}H\\OH{\cdot}H\end{matrix} \xrightarrow{O_2} C\begin{matrix}OH{\cdot}H{\cdot}O\\OH{\cdot}H{\cdot}O.\end{matrix}\begin{matrix}H{\cdot}O\\H{\cdot}O\end{matrix} + \begin{matrix}CO{\cdot}OH\\|\\COOH\end{matrix} \rightarrow 2CO_2 + 2H_2O.$$

The addition of *M*/1000-potassium iodide, however, had no effect on the reaction velocity.

surface phase becomes deficient in oxygen or acid by displacement. The maximum velocity, which is attained when the surface is covered with acid and oxygen in suitable stoicheiometric proportions, is identical for the two gas pressures examined; this may be taken as proof that we are in reality dealing with a constant area of catalytic surface which is almost completely saturated with the two reactants, the displacement of the maximum towards higher oxalic acid concentrations at higher oxygen pressures representing the

FIG. 2.

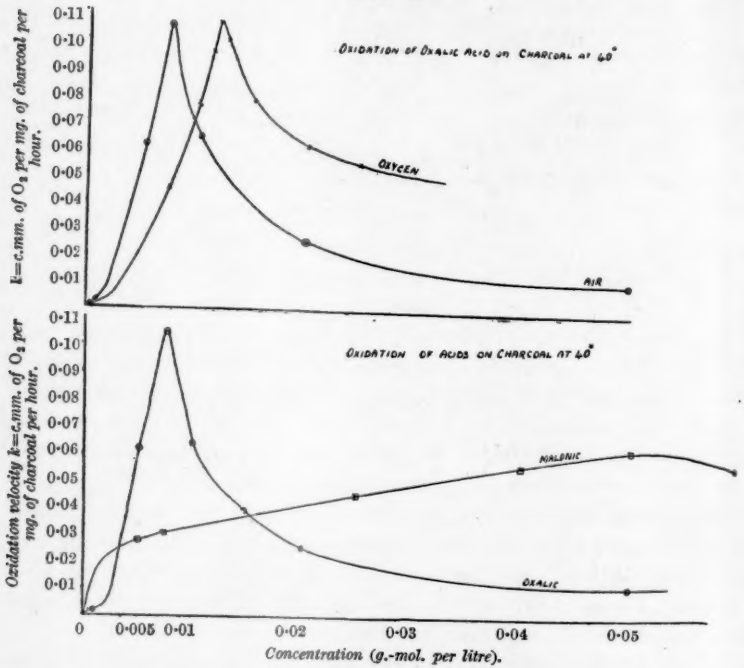


FIG. 1.

displacement of adsorbed oxalic acid by oxygen. The optimum concentration of acid under constant gas pressure does not appear to alter for an elevation of temperature of 10°, an indication that the adsorptive unions between the reactants and charcoal are relatively strong and do not differ sensibly from one another. The adsorption isotherms for malonic and oxalic acids were determined for the charcoal, and the surface concentrations at the point of optimum velocity of oxidation were found to be as follows. The specific activities of the acids as measured by the value of $k_{max.}$ are inversely proportional to the amounts adsorbed.

Acid.	$k_{max.}$	C at $k_{max.}$ molarity.	Amount adsorbed (x), g.-mol. per mg. of charcoal.	$k_{max.} \times x$.
Oxalic	0·105	0·0075	$3{\cdot}4 \times 10^{-7}$	$3{\cdot}57 \times 10^{-8}$
Malonic	0·060	0·050	$5{\cdot}9 \times 10^{-7}$	$3{\cdot}54 \times 10^{-8}$

The extent of surface catalytically active was determined by the addition of amyl alcohol as poison until the reaction ceased, the adsorption of the amyl alcohol from the solution being determined by means of the surface tension (drop-weight method). When the catalytic activity ceased completely, owing to the selective adsorption of the alcohol, the amount adsorbed per mg. of charcoal was $4{\cdot}2 \times 10^{-7}$ mol. Hence the number of catalytically active atoms per mg. is of the order $4{\cdot}2 \times 10^{-7} \times 6{\cdot}06 \times 10^{23} = 2{\cdot}55 \times 10^{17}$ atoms, representing a fraction of the total area of $2{\cdot}55 \times 10^{17} / 6{\cdot}30 \times 10^{17} = 40{\cdot}5\%$.*

No very definite conclusions, however, can be drawn from the above data as to the surface concentrations of the two reactants on the active area, since the oxalic and malonic acids, when adsorbed on the active areas in suitable concentrations for optimum velocity of reaction, are doubtless adsorbed to some extent on the less active areas as well.

The determinations of the oxygen absorbed and of the carbon dioxide evolved, for very dilute solutions of oxalic acid, may be employed for calculating the effect of increasing oxalic acid concentration on the autoxidation as is indicated in Fig. 3. The autoxidation (curve 2) is gradually poisoned by the adsorbed oxalic acid; thus this substance poisons the autoxidisable areas in a manner analogous to that of other adsorbed solutes.

It is thus clear that very active areas may readily be distinguished from feebly active areas by selective poisoning, provided that the poison is adsorbed only by the active areas. For this purpose it is desirable to utilise small concentrations of strongly adsorbed poisons (although an upper limit to the strength of union poison–substrate is set by the necessity for obtaining true equilibrium in a relatively short space of time). Areas differing but little in activity can be distinguished from one another only by employing a number of poisons with different adsorption coefficients.

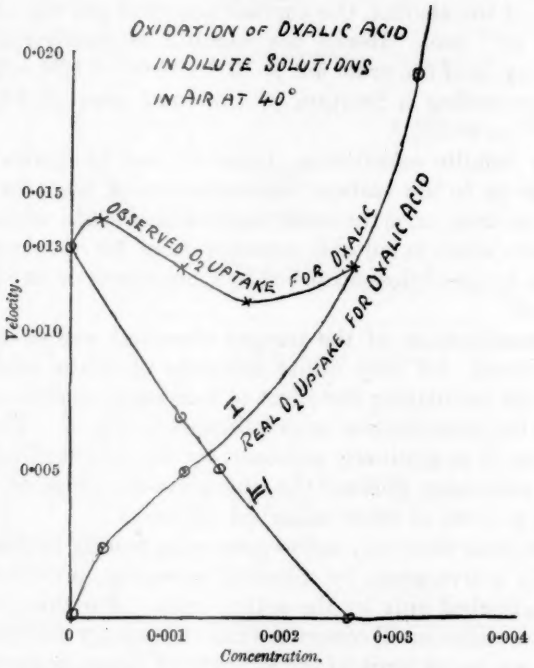
Interpretation of the Curves.

The definite maximum exhibited in the oxidation of oxalic acid at the surface of charcoal with increasing acid concentration indicates that both reactants must be adsorbed on a limited area of

* This evidently represents a maximum for the catalytically active area, since poisoning is not necessarily quite selective in its action.

surface. If we denote the rate at which oxygen strikes the surface, which rate will be proportional to the oxygen pressure, by P_{O_2}, and the rate at which oxalic acid strikes the surface by C_{ox}, when equilibrium is established a fraction, θ_1, of the surface will be covered with oxygen and a fraction, θ_2, covered with oxalic acid, the remainder, θ, being covered with water which the reactants can displace. If v_1 and v_2 be the specific rates of desorption of the reactants and α_1 and α_2 the coefficients of reflection, then, on the

FIG. 3.



assumption that the oxygen molecule occupies two elementary spaces on the lattice and the oxalic acid but one, at equilibrium we obtain

$$(1)\quad \alpha_1 P_{O_2}\theta^2 = v_1\theta_1^2 \text{ and } \alpha_2 C_{ox}\theta = v_2\theta_2 \quad . \quad . \quad . \quad . \quad (2)$$

The rate of chemical action between oxalic acid and oxygen on the surface will be

$$dx/dt = k\theta_1\theta_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Also

$$\theta + \theta_1 + \theta_2 = 1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Hence, eliminating θ_1, θ_2, and θ,

$$\frac{dx}{dt} = k\left(\sqrt{\frac{\alpha_1 P_{O_2}}{v_1}}\right)\left(\frac{\alpha_2}{v_2}.C_{ox}\right)\theta^2 = \frac{k'\sqrt{P_{O_2}}C_{ox}}{(1 + m\sqrt{P_{ox}} + nC_{ox})^2}$$

For small concentrations of oxygen and oxalic acid this equation reduces to $dc/dt = k\sqrt{P_{O_2}}C_{OX}$. As the oxygen pressure increases and the oxalic acid concentration remains small, we obtain $dc/dt = kC_{OX}/\sqrt{P_{O_2}}$. This portion of the curve is experimentally realised at the commencement.

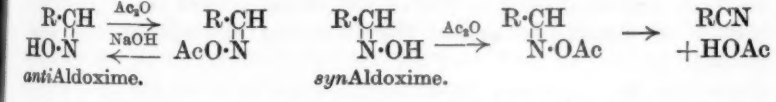
At the other end of the curve, where the surface is approaching saturation in oxalic acid and the oxygen pressure is relatively low, the expression reduces to $dx/dt = k\sqrt{P_{O_2}}/C_{OX}$, the form obtained by Warburg and his co-workers; this is exemplified in the curves in the region for high oxalic acid concentrations; whilst when the oxygen pressure and oxalic acid concentration are commensurate with each other and are both large the curve evidently passes through a maximum value independent of P_{O_2} or C_{OX}, a phenomenon likewise apparent from the experimental data.

UNIVERSITY OF CAMBRIDGE. [*Received, April 16th*, 1925.]

CLXXXV.—*The Isomerism of the Oximes. Part XXII. The Configuration of the Aldoximes.*

By OSCAR L. BRADY and GERALD BISHOP.

THE configuration of the aldoximes, as generally accepted, is based on a method of determination first suggested by Hantzsch (*Ber.*, 1891, **24**, 13), though the procedure has been subsequently somewhat modified. It depends upon the fact that acetic anhydride at a temperature not above 30° converts both isomerides into acetyl derivatives, and that on subsequent treatment of these compounds with dilute sodium hydroxide one is converted into the nitrile, whilst the other is hydrolysed with the reformation of the original oxime; the term *syn* was assigned to the former class, since it was held that the elimination of acetic acid would take place more readily if the H and OAc were contiguous, whilst the term *anti* was given to the latter compounds.

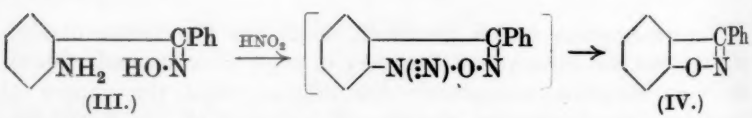


The assumption which Hantzsch made has the virtue of simplicity, but the subsequent discovery of *trans*-addition and -elimination in ethylenic compounds has demonstrated the danger of assuming *cis*-elimination merely on account of its simplicity. Recently the case for *trans*-elimination has been put by several workers, particularly by Beckmann, Liesche, and Correns (*Ber.*,

1923, **56**, 341) on theoretical grounds and by von Auwers and Ottens (*Ber.*, 1924, **57**, 446) from a study of the optical properties of the aldoximes and their ethers. For similar reasons, doubt has been thrown by Meisenheimer and his co-workers (*Ber.*, 1921, 54, 3195, 3206; 1924, **57**, 276, 282, 289) on the view that in the Beckmann change of ketoximes the vicinal groups are interchanged. They found that 3 : 4 : 5-triphenyl*iso*oxazole (I), on treatment with ozone followed by water, gave benzoyl-β-benzilmonoxime (II), which could be hydrolysed to β-benzilmonoxime and could be regenerated by benzoylation of the β-oxime. Now the configuration (II) is that usually assigned, on the basis of the Beckmann change, to benzoyl-α-benzilmonoxime, and it is accordingly suggested that the configuration of these compounds should be reversed and that the Beckmann change takes place in a *trans* and not a *cis* sense.

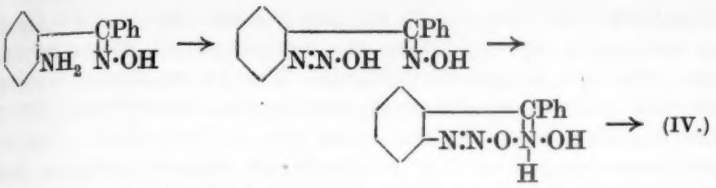
(I.) $C_6H_5\cdot C(N\cdot O\cdot C\cdot C_6H_5)\!-\!C\cdot C_6H_5 \longrightarrow C_6H_5\cdot C(N\cdot O\cdot CO\cdot C_6H_5)\!-\!CO\cdot C_6H_5$ (II.)

This argument is, however, open to criticism in view of the peculiar behaviour of oximes on benzoylation. The stable cinnam*syn*- and *o*-methoxycinnam*syn*-aldoximes are converted into the benzoyl derivatives of the corresponding *anti*aldoximes on benzoylation (Brady and Thomas, J., 1922, **121**, 2104; Brady and Grayson, J., 1924, **125**, 1419) and in a subsequent paper it will be shown that this reaction is a general one. Although the doubt has been partly removed by Meisenheimer, some still exists regarding the constitution of the compound obtained by the benzoylation of α-benzilmonoxime owing to the fact that the oxime cannot be regenerated therefrom by hydrolysis. Consequently, although the above work seems conclusive, it cannot be accepted without reservation. A second instance is adduced by Meisenheimer in support of his views. *o*-Aminobenzophenoneoxime exists in two forms, only one (III) of which gives the benz*iso*oxazole (IV) on diazotisation. Here again the results are contrary to those indicated by a *cis*-Beckmann change, since (III) gives the anilide of anthranilic acid. The following mechanism was suggested:



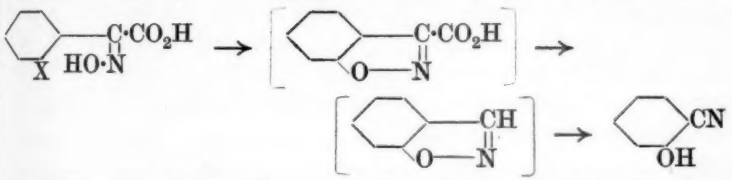
(III.) (IV.)

but the reaction might be interpreted in another way using the alternative configuration:

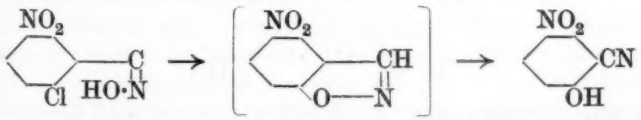


Meisenheimer tried to use benzo*iso*oxazole formation from the oximes of ortho-halogen substituted benzophenones to determine their configuration, but was unable to obtain two isomerides of *o*-chloro- or *o*-bromobenzophenoneoxime (compare also von Auwers and Jordan, *Ber.*, 1925, **58**, 26).

No fresh evidence of a purely chemical nature has, however, been forthcoming concerning the configuration of the aldoximes and it seemed likely that the action of alkalis on ortho-halogen substituted aldoximes might afford information. In this case the benzo*iso*oxazole cannot be isolated, undergoing tautomeric change to the hydroxynitrile. For example, this compound was obtained in attempts to prepare the benzo*iso*oxazole by the following reaction :



where X = Br or NO_2 (Russanow, *Ber.*, 1892, **25**, 3297; V. Meyer, *Ber.*, 1893, **26**, 1256). Similarly, Bone (J., 1893, **63**, 1346) obtained 5-nitrosalicylonitrile by heating 5-nitro-*o*-chlorobenz*anti*aldoxime with 22% sodium carbonate for 2—3 hours at 120°.

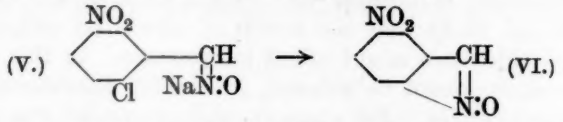


(Compare also the similar behaviour of the *iso*oxazoles, Claisen and Stock, *Ber.*, 1891, **24**, 130; Claisen, *Ber.*, 1903, **36**, 3664.)

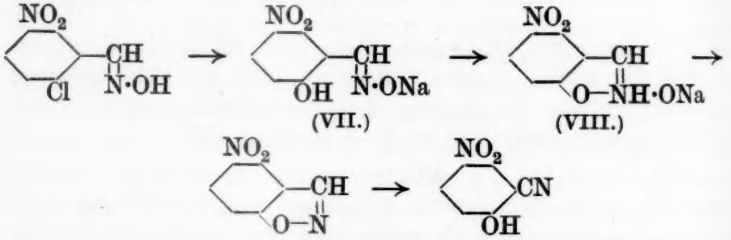
Neither of the isomeric *o*-chlorobenzaldoximes reacts sufficiently readily to be satisfactory for the purpose, but the introduction of a nitro-group renders the chlorine more reactive, and the study of the isomeric 2-chloro-5-nitrobenzaldoximes has lead to interesting results. The *anti*-isomeride (according to Hantzsch) does not give any ionisable chlorine when heated at 50° for 4 hours with 0·25*N*-sodium hydroxide, whilst under the same conditions the *syn*-isomeride yields 27% of its chlorine in an ionised form after 1 hour, 45% after 2 hours, and 53% after 4 hours. Boiling with

N-sodium hydroxide for 30 minutes brought about slight change in the *anti*-isomeride, whilst the *syn*-compound was completely converted into 5-nitrosalicylonitrile. There is no doubt, therefore, that the so-called *syn*-isomeride is more readily converted through the unstable benzo*iso*oxazole into the hydroxy-nitrile than the *anti*-isomeride. Since it is reasonable to suppose that ring formation will occur more readily when the hydroxyl group is vicinal to the halogenated benzene ring, this result involves the reversal of the configuration of the aldoximes in accordance with the views of Meisenheimer, Beckmann, and von Auwers.

Two alternatives, however, need consideration. The sodium salt of the so-called *syn*-oxime may be represented as (V), the elimination of sodium chloride then giving (VI);

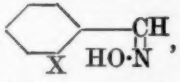


but it does not seem likely that this compound would give the hydroxy-nitrile so readily. The second is that the halogen is first removed by hydrolysis, giving (VII); then follow a kind of salt formation (VIII) and subsequent loss of water to give the benzo-*iso*oxazole and hence the hydroxy-nitrile as suggested above for the aminobenzophenoneoxime.



This seems unlikely, since the halogen is not readily removed by hydrolysis from the *anti*-oxime nor from 2-chloro-5-nitrobenzonitrile nor from 2-chloro-5-nitrobenzoic acid.

Any isomeric change, apart from tautomerism, in the oximes would take place in the direction *syn* to *anti* or reactive to unreactive form, for in our work on the aldoximes no indication of a change in the reverse direction under these conditions has been observed in the many cases of substituted benzaldoximes investigated. This change probably accounts for the slowing of the reaction and its apparent departure from the law of mass action. The only point in doubt in this connexion is that during the change *syn* to *anti* the molecule may be in a particularly reactive state.

As a result of this work it appears doubtful whether Hantzsch's assumption that *cis*-elimination of acetic acid takes place from the acetyl derivatives of the aldoximes can be maintained, and, taken in conjunction with the investigations of Meisenheimer, there are considerable grounds for suggesting that the configurations of all these compounds should be reversed. There is also some collateral evidence in support of such reversal (which will be discussed in subsequent communications), notably perhaps the difficulty often experienced in obtaining the so-called *syn*-isomerides of ortho-substituted benzaldoximes; if these have the structure  , their non-formation may be due to steric hindrance. Such a reversal, at the present time, would lead to great confusion, and further work is being undertaken which may lead to a reconsideration. For this reason, we propose to adopt in future the following convention. The aldoximes will be designated α- and β-, the α-oxime being that which on treatment with acetic anhydride at 30° gives an acetyl derivative which on hydrolysis regenerates the original oxime, whilst the β-oxime is that which under the same conditions gives the nitrile or the corresponding acid; α-acyl derivatives are those which on hydrolysis regenerate the oximes, β-acyl derivatives those which give the nitrile or acid; α-*O*-ethers are those prepared from α-oximes, β-*O*-ethers those prepared from β-oximes, there being at present no method by which the configuration of these compounds can be directly ascertained.

Experimental.

α-2-*Chloro*-5-*nitrobenzaldoxime*.—A mixture of 2-chloro-5-nitrobenzaldehyde (5 g.; prepared by the nitration of *o*-chlorobenzaldehyde; Erdmann, *Annalen*, 1893, **272**, 153), sodium acetate (5 g.), and hydroxylamine hydrochloride (2 g.) in alcohol (100 c.c.) was heated for 2 hours under reflux. The oxime was precipitated with water and crystallised from benzene. Its configuration was determined by the Hantzsch method—dissolution in acetic anhydride at room temperature and shaking with sodium carbonate; the solid separating was crystallised from dilute alcohol, when *α-acetyl-2-chloro-5-nitrobenzaldoxime* was obtained as a pale buff, microcrystalline powder, m. p. 110° (Found: N, 11·7. $C_9H_7O_4N_2Cl$ requires N, 11·5%). When this compound was warmed with 2*N*-sodium hydroxide until it dissolved, and the solution saturated with carbon dioxide, the original oxime was obtained.

β-2-*Chloro*-5-*nitrobenzaldoxime*.—When hydrogen chloride was passed into a chloroform or ethereal solution of the α-oxime, no

hydrochloride was formed (compare 2 : 4-dinitrobenzaldoxime: Wentworth and Brady, J., 1920, **117**, 1040; Brady and Manjunath, J., 1924, **125**, 1066). Transformation was, however, brought about by Dunstan and Thole's method, but it was essential to use sufficient hydrochloric acid to ensure complete solution. The α-oxime (4 g.) was ground with concentrated hydrochloric acid (100 c.c.), the mixture cooled in ice and saturated with hydrogen chloride. The clear solution was poured into a large excess of 2*N*-sodium carbonate. The dried precipitate, after crystallising three times from benzene, gave β-2-*chloro*-5-*nitrobenzaldoxime* in very pale yellow needles, m. p. 176° (Found: N, 14·1. $C_7H_5O_3N_2Cl$ requires N, 14·0%). This was oriented in a similar way to the α-oxime; the acetyl derivative was not, however, isolated pure, but was hydrolysed at once, when ammonia and 2-chloro-5-nitrobenzoic acid were obtained.

Action of Alkali on α- and β-2-Chloro-5-nitrobenzaldoximes.—A solution of the α-oxime (0·25 g.) in *N*-sodium hydroxide (10 c.c.) was boiled under reflux for 30 minutes, cooled, and saturated with carbon dioxide, when 0·15 g. of the original oxime was recovered. The filtrate on acidification gave a small amount of 5-nitrosalicyclic acid. The β-oxime, treated similarly, gave with carbon dioxide a precipitate which, after crystallisation from water, was identified as 5-nitrosalicylonitrile, whilst the solution on acidification gave a small amount of 5-nitrosalicylic acid. With 0·5*N*-sodium hydroxide at 50°, the α-oxime gave no chlorine ions after 4 hours. In the case of the β-oxime 0·632 g. was dissolved in 100 c.c. of 0·25*N*-sodium hydroxide at 50° and kept at that temperature in a thermostat; 25 c.c. were removed from time to time, acidified with dilute nitric acid, and the ionised halogen at once determined by Volhard's method. After 1 hour 27% of the halogen was in the ionised form, after 2 hours 45%, and after 4 hours 53%.

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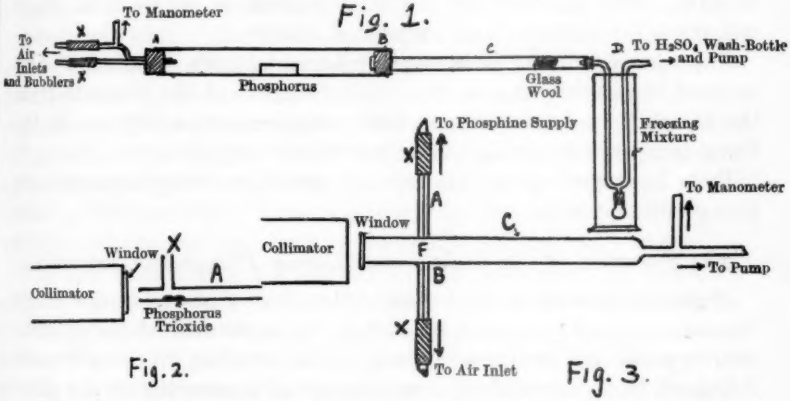
CLXXXVI.—*A Spectroscopic Study of the Combustion of Phosphorus Trioxide and of Hydrogen Phosphide.*

By HARRY JULIUS EMELÉUS.

THE spectroscopic investigation of the light emitted in many chemical reactions is a direct way of examining the mechanism of chemical change, although an extensive application of this method is hindered by the complex nature of most processes of

combustion and by our still scanty knowledge of the origin of spectra. Flames may be arbitrarily divided into two groups. The first comprises ordinary hot flames, in which light emission may be influenced by little-known temperature factors. The second is the class of phenomena termed chemiluminescence, which includes chemical reactions emitting light without any considerable rise in temperature (*e.g.*, below 200°). In this case it is more certain that the radiation has its origin in the chemical process, and the interpretation of the spectra observed is consequently more readily carried out.

The oldest recorded example of chemiluminescence is the slow oxidation of phosphorus at room temperature. The light emitted was found by Centnerszwer and Petrikaln (*Z. physikal. Chem.*, 1912, **80**, 235) to give a continuous spectrum in the visible region,



and to show five bands (or groups of lines) in the ultra-violet at about $\lambda = 3270$, 2600, 2530, 2470, 2390 Å.U. This light gives essentially the same band spectrum as that obtained from phosphorus burning normally, or under reduced pressure with a flame temperature of 125° (Emeléus and Downey, J., 1924, **125**, 2491). In the experiments described below, the light from phosphorus trioxide slowly oxidising at the ordinary temperature and the flame of pure hydrogen phosphide burning under various conditions have been investigated, since they exhibit certain chemical anomalies in common with the slow oxidation of phosphorus, which are more fully discussed subsequently.

Preparation of Material.—The method of preparation of phosphorus trioxide described by Thorpe and Tutton (J., 1890, **57**, 545) was modified as follows :

Phosphorus was burnt *under reduced pressure* in the hard glass tube A B (2·5 cm. × 40 cm.) (Fig. 1). The air inlets were controlled

by screw clips at X X, and bubblers containing water were attached. A mercury manometer, connected as shown, was used to record the pressure. The tube C for condensing phosphorus pentoxide, and the U-tube D for collecting the product were as described by Thorpe and Tutton, but C was maintained at 50° by several Bunsen burners instead of by the use of a special hot water-jacket. Such a quantity of phosphorus (about 50 g.) was used that the molten material did not approach within 5 cm. of A. The best yields resulted when the flame was burning as a vertical yellow disk at a pressure of 30—40 cm. of mercury.

About 4 g. of phosphorus trioxide were produced consistently from 40—50 g. of phosphorus in 2—3 hours by this method, the apparatus requiring little attention. The product was volatilised from reduced copper gauze at 100—140° in a stream of dry carbon dioxide. The material so obtained melted at 22·0—22·5° to a colourless liquid, free from suspended matter.

The relatively large yield of phosphorus trioxide obtained by this method is possibly due to the rapid removal of the trioxide from the hot zone (it decomposes at 200°), coupled with a decrease in the flame temperature owing to the limited air supply.

Pure hydrogen phosphide was prepared by dropping water on phosphonium iodide.

The Spectrum of the Light from Glowing Phosphorus Trioxide.

Preliminary work showed that (i) the glow of phosphorus trioxide does not normally occur at its surface, as in the case of phosphorus, but appears as luminous pulses, often starting at considerable distances from the oxide, (ii) water vapour is essential to the glow, and the pulses occur more readily in presence of a little liquid water.

The apparatus finally adopted is illustrated in Fig. 2. The glass tube A, of 3 mm. internal diameter, was supported in correct alignment with the collimator slit, which was protected by a quartz window 2 mm. thick. The tube was first moistened, and one or two drops of molten phosphorus trioxide were introduced at X. It was warmed electrically to 30—40° by a resistance mat placed underneath, and a series of bright pulses was maintained by a slight draught. The tube was washed and recharged as each successive quantity of oxide became exhausted (generally after about 40 minutes). An exposure of 280 hours was recorded on a rapid plate, a copper arc spectrum being used for reference purposes, and the plate was sensitised before development by Wood's method (*Astrophys. J.*, 1908, **27**, 379).

The spectrum is identical with that obtained in the case of glowing phosphorus (Emeléus and Downey, *loc. cit.*). The five

ultra-violet bands are fainter, but their relative intensities agree with those in the glow spectrum of phosphorus, as far as can be judged without elaborate photometric measurements.

The Spectrum of pure Hydrogen Phosphide burning spontaneously under Reduced Pressure in Air.

The apparatus shown in Fig. 3 was used. The tube C, of about 1 cm. internal diameter, had two capillary tubes, A, B, serving as inlets for the phosphide and air, sealed at about 5 cm. from the ground end, to which a quartz window, 2 mm. thick, was attached with wax. Connexion was also made to a water-pump and mercury manometer as shown. Ignition of the phosphide occurred spontaneously as the two gas streams entered the region of reduced pressure. The rate of supply of the gases was controlled by screw clips on the rubber connexions at X, X, and was so adjusted that a steady greenish-white flame resulted at F, the pressure being 3—8 cm. of mercury. Owing to the formation of a red decomposition product, the apparatus was cleaned and replaced every hour. An exposure of 20 hours was made, the further treatment of the plate being as described before. The temperature of the flame, measured by a thermometer inserted in place of the quartz window, varied between 160° and 230°. Luminosity will occur even at 40—60° if the velocities of the two gas streams are small, but it is very feeble.

The spectrum shows all the ultra-violet bands of the spectrum of glowing phosphorus and of phosphorus trioxide, and no others. It closely resembles that of phosphorus burning under reduced pressure in air (Emeléus and Downey, *loc. cit.*). In the spectra of the low-temperature flames the band at about $\lambda = 3270$ Å.U. is relatively more intense than in the glow spectra. This point will be referred to later.

If the vapour of acetone or ether is allowed to mix with the ingoing air when the phosphide flame is burning steadily at about 50°, it first produces an intermittent luminescence, the pulses then become less frequent and finally cease. When the supply of inhibiting vapour is stopped, the same phenomena are observed in the reverse order. Ether and acetone are particularly active poisons: the latter dimmed a flame even at 180°. Benzene, chloroform, coal gas, and ammonia act less effectively. A closer examination of this interesting phenomenon is being made.

The Spectrum of Hydrogen Phosphide burning at a Jet in Oxygen at Atmospheric Pressure.

With an exposure of 5 minutes the band at $\lambda = 3270$ Å.U. is observed, in addition to a strong and apparently continuous back-

ground. With a 15-minute exposure the four bands at $\lambda = 2600$, 2530, 2470, 2390 Å.U. are visible, and also two bands at about $\lambda = 3060$, 2800 Å.U. The latter are generally ascribed to water, and their presence is to be expected from the nature of the reaction. They are not excited in the low-temperature combustion of hydrogen phosphide, which is in agreement with van de Stadt's observation that free hydrogen is formed (compare van 't Hoff, "Studies in Chemical Dynamics," 1896).

Discussion of Results.

A very close analogy exists between the phenomena of the slow luminous oxidations of phosphorus and of phosphorus trioxide. Both can occur at room temperature, and are accompanied by the production of ions and ozone (compare Downey, J., 1924, **125**, 347). Rinde (*Arkiv Kemi, Min., Geol.*, 1918, **7**, No. 7) found that the ions produced in the latter case have approximately the same mobilities and coefficient of recombination as the ions from oxidising phosphorus (Bloch, *Ann. Chim. Phys.*, 1905, **4**, 25). Scharff (*Z. physikal. Chem.*, 1908, **62**, 179) pointed out that those substances which inhibit the oxidation and luminosity of phosphorus act in precisely the same way in the case of phosphorus trioxide. His contention that a boundary pressure exists, similar to that which is well known in the case of phosphorus, above which luminosity will not occur in pure oxygen, is not confirmed by Rinde (*loc. cit.*). In the author's experience these experiments give such inconsistent results that a final conclusion is not yet justifiable.

The glow of phosphorus and that of phosphorus trioxide differ sharply with regard to the necessity for the presence of water. Phosphorus glows readily in air or rarefied oxygen dried by passage over phosphorus pentoxide, but no luminosity occurs up to 60° for phosphorus trioxide under these conditions. Moreover, drying by strong sulphuric acid causes a big decrease in the brightness of the glow in the latter case. A slow non-luminous oxidation of phosphorus trioxide to phosphorus pentoxide has, however, been shown to occur when absence of water vapour prevents luminosity (Rinde, *loc. cit.*).

The suggestion that water plays an essential part in the luminous oxidation of phosphorus trioxide was made by Schenck, Mihr, and Banthien (*Ber.*, 1906, **39**, 1506). Rinde put forward the hypothesis that hydrogen phosphide is first formed by interaction of phosphorus trioxide and water, and is then oxidised with luminescence. Since phosphorus trioxide is known to be formed in the slow oxidation of phosphorus, the same view could be applied to the case of glowing phosphorus, provided water were present. It is

known, moreover, that spontaneously inflammable hydrogen phosphide results from the interaction of phosphorus trioxide and water at 90°, and this reaction might be supposed to occur to the necessary limited extent at room temperature. Indirect evidence that such is the case is afforded by the behaviour of hydrogen phosphide outlined below, but a direct demonstration of the reaction is still lacking.

Hydrogen phosphide and oxygen react only very slowly at ordinary pressures, but when the pressure is reduced an explosion occurs (compare van 't Hoff, *op. cit.*). Also, experiments described above show that certain substances can inhibit the ignition of the phosphide when the pressure of phosphide–air mixtures is reduced, these substances being all inhibitors of the glows of phosphorus and of its trioxide. In addition, the pulsating effect produced by inhibiting substances on the flame of hydrogen phosphide seems closely parallel to Lord Rayleigh's observations with phosphorus (*Proc. Roy. Soc.*, 1921, *A*, **99**, 372, *et seq.*).

The foregoing review of the anomalies which are in some measure common to the low-temperature oxidation of phosphorus and of its two compounds appears to be in complete agreement with the spectroscopic results. That these three oxidation processes should give the same light emission, coupled with the fact that they have so much else in common, renders it very probable that there is something produced in each case responsible for the chemical peculiarities, and intimately connected with the luminosity. The spectroscopic evidence does not justify the assumption that the chemical processes themselves are identical: further chemical evidence is needed to decide that. It does, however, show that some excited system is produced in each of the chemical reactions studied, which radiates the ultra-violet band spectrum observed.

There are a few relevant points with regard to the light itself. The apparently continuous visible radiation in each case has yet to be accounted for. From the fact that a band spectrum is produced, and not a line spectrum, it may be concluded that this is of molecular origin. The band at about $\lambda = 3270$ Å.U. was observed by Hartley (*Phil. Trans.*, 1894, **185**, 168) on volatilising phosphorus pentoxide in the oxy-hydrogen flame, and Petrikaln (*Z. Physik*, 1924, **22**, 119) has drawn attention to the presence of the five bands in the spectrum produced by phosphorus pentoxide in the carbon arc. These observations render it probable that the molecule responsible is that of phosphorus or of a phosphorus oxide. If it were possible to analyse the bands and so find the moment of inertia of the radiating system, its nature might be settled, but there appears to be no immediate prospect of this.

As stated above, the band at about $\lambda = 3270$ Å.U., compared

with the remaining four bands, is relatively less intense in the glow spectra of phosphorus and of its trioxide than in that of phosphorus or hydrogen phosphide burning under reduced pressure. The reason for this striking result can only be surmised: it may be that this band is due to a different chemical compound from the others, but it could equally well arise from the influence of physical conditions on the occurrence of the various quantum transitions.

Summary.

1. A modification of Thorpe and Tutton's method of preparing phosphorus trioxide is described.

2. A spectroscopic study of the light from glowing phosphorus trioxide, from pure hydrogen phosphide burning spontaneously in air under reduced pressure, and from the pure phosphide burning in oxygen, has been made. In each case the ultra-violet band spectrum is identical with that of glowing phosphorus, and of the element burning normally. A variation in the relative intensity of the bands with the conditions has been noted.

3. Certain substances which inhibit the glow of phosphorus and of phosphorus trioxide can prevent the ignition of a hydrogen phosphide–air mixture when the pressure is reduced.

4. It is suggested that the low-temperature combustions of phosphorus, phosphorus trioxide, and hydrogen phosphide involve some common stage responsible for the chemical anomalies and intimately bound up with the characteristic light emission.

The author wishes to express his gratitude to Professor H. B. Baker, F.R.S., in whose laboratory this work was carried out, for his kind interest at all times. He is also much indebted to Professor A. Fowler, F.R.S., for advice in the interpretation of the spectroscopic results. The work has been rendered possible by a maintenance grant from the Department of Scientific and Industrial Research, for which the author desires to express his thanks.

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CLXXXVII.—*The Action of Phosphorus Pentachloride on* 2-iso*Nitroso*-1-*hydrindones.*

By ROBERT DOWNS HAWORTH and HERBERT SHEPPARD PINK.

IN the preparation of 4 : 5-dimethoxyhomophthalic acid from an ethereal suspension of 2-*iso*nitroso-5 : 6-dimethoxy-1-hydrindone and phosphorus pentachloride, at the stage at which the product

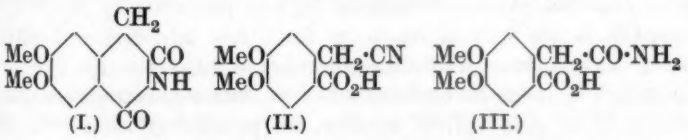
was poured into ice-water, the ethereal solution contained a substance which gave the required acid on hydrolysis but was not further investigated (Perkin and Robinson, J., 1907, **91**, 1082); the authors suggested, however, that it might be 4 : 5-dimethoxyhomophthalimide (I), produced by a Beckmann rearrangement of the *iso*nitroso-compound.

We have now isolated the intermediate product and found that, although its composition is that of dimethoxyhomophthalimide, its properties differ in some respects from those characteristic of homophthalimide derivatives; for example, the substance is readily soluble in organic solvents and in sodium bicarbonate, and is rapidly hydrolysed on warming with sodium hydroxide or dilute sulphuric acid. It therefore seemed probable that the substance is 2-*carboxy*-4 : 5-*dimethoxyphenylacetonitrile* (II). This view was confirmed by the observation that alkaline hydrogen peroxide converts it into 4 : 5-*dimethoxyhomophthalamic acid* (III), which is then converted into 4 : 5-dimethoxyhomophthalimide (I) on heating. This is an insoluble, high-melting substance identical with the product of the action of heat on ammonium 4 : 5-dimethoxyhomophthalate.

Similarly, the intermediate compound produced by the action of phosphorus pentachloride on 2-*iso*nitroso-1-hydrindone is *o*-carboxyphenylacetonitrile, identical with the acid obtained by the action of potassium cyanide on phthalide (Wislicenus, *Annalen*, 1886, **233**, 102). It is converted by the action of alkaline hydrogen peroxide into homophthalamic acid, and this yields homophthalimide on being heated at 200°.

2-*Carboxy*-4 : 5-*methylenedioxyphenylacetonitrile* (as II) has been obtained from 2-*iso*nitroso-5 : 6-methylenedioxy-1-hydrindone, and from it the corresponding *homophthalamic acid* (as III) and *homophthalimide* (as I) have been prepared.

The yields of the *o*-carboxyphenylacetonitriles obtained under the conditions outlined are good and this method appears to be the most convenient for the preparation of these substances.



EXPERIMENTAL.

o-*Carboxyphenylacetonitrile*.—2-*iso*Nitroso-1-hydrindone and phosphorus pentachloride were allowed to react under the conditions described by Perkin and Robinson (*loc. cit.*). The reaction mixture

was poured on to ice, and the *o*-carboxyphenylacetonitrile collected; a further quantity was extracted from the filtrate with ether. It crystallised from hot water in colourless needles, m. p. 126° (decomp.), and did not depress the m. p. (124°; decomp.) of a sample prepared by Wislicenus's method (*loc. cit.*) and thrice crystallised from water.

Homophthalamic acid was prepared by treating a solution of *o*-carboxyphenylacetonitrile (7 g.) in a very slight excess of *N*-sodium hydroxide with a 3% solution of hydrogen peroxide at room temperature for 6 hours and acidifying the product with concentrated hydrochloric acid. The precipitated homophthalamic acid (7 g.), after being washed with water, crystallised from alcohol in colourless needles, m. p. 186°.

Homophthalimide was prepared in quantitative yield by heating homophthalamic acid at 200° until the evolution of water was complete. The residue crystallised from glacial acetic acid in pale yellow needles, m. p. 233°.

2-*Carboxy*-4 : 5-*dimethoxyphenylacetonitrile* (II) was prepared from dimethoxy*iso*nitrosohydrindone in the same way as its analogue. After two crystallisations from aqueous alcohol, the acid was obtained in long, colourless needles, m. p. 164—165° (decomp.) (Found : C, 59·8; H, 5·0. $C_{11}H_{11}O_4N$ requires C, 59·7; H, 5·0%). It is sparingly soluble in ether or hot water, but readily soluble in alcohol or acetic acid. When boiled with sodium hydroxide solution or with dilute sulphuric acid, it gives 4 : 5-dimethoxyhomophthalic acid, which crystallises from alcohol in needles, m. p. 223—224° (Perkin and Robinson, *loc. cit.*, give 215°); low figures are always obtained unless the intermediate carboxyphenylacetonitrile is purified. However, the homopiperonylimide, m. p. 178°, of the acid melting at 215° is identical with that prepared from the pure acid, m. p. 224°.

4 : 5-*Dimethoxyhomophthalamic acid* (III), prepared in the same way as its analogue, is insoluble in water, and crystallises from alcohol in colourless prisms, m. p. 204° (decomp.) (Found : C, 55·3; H, 5·5. $C_{11}H_{13}O_5N$ requires C, 55·2; H, 5·4%).

4 : 5-*Dimethoxyhomophthalimide* (I) was prepared by heating the homophthalamic acid at its m. p. for a few minutes, and also by heating ammonium 4 : 5-dimethoxyhomophthalate at 210°. It is sparingly soluble in organic solvents, but separates from glacial acetic acid in pale yellow needles, m. p. 245° (Found : C, 59·6; H, 5·0. $C_{11}H_{11}O_4N$ requires C, 59·7; H, 5·0%).

2-*Carboxy*-4 : 5-*methylenedioxyphenylacetonitrile*, prepared in the same way as its analogues, is sparingly soluble in water, ether, benzene, or alcohol, but crystallises from much alcohol in minute prisms, m. p. 195—196° (decomp.) (Found : C, 58·6; H, 3·5.

$C_{10}H_7O_4N$ requires C, 58·5; H, 3·4%). It is hydrolysed to 4 : 5-methylenedioxyhomophthalic acid, m. p. 236°, on warming with dilute acids or alkalis.

4 : 5-*Methylenedioxyhomophthalamic acid*, obtained in the same way as homophthalamic acid, crystallises from much alcohol in small rectangular prisms which soften at 230°, darken at 280°, and melt at 295°, which is the melting point of the corresponding homophthalimide (Found : C, 53·9; H, 4·1. $C_{10}H_9O_5N$ requires C, 53·8; H, 4·0%).

4 : 5-*Methylenedioxyhomophthalimide*, obtained by heating the homophthalamic acid at 200° for 15 minutes, crystallises from glacial acetic acid in yellow prisms, m. p. 295° (darkening at 280°) (Found : C, 58·6; H, 3·6. $C_{10}H_7O_4N$ requires C, 58·5; H, 3·4%).

The authors wish to express their thanks to the Commissioners of the 1851 Exhibition and to the Salters' Institute of Industrial Chemistry for scholarships, and to the Research Fund Committees of the Royal Society and the Chemical Society for grants.

THE DYSON PERRINS LABORATORY,
OXFORD. [*Received, May 2nd*, 1925.]

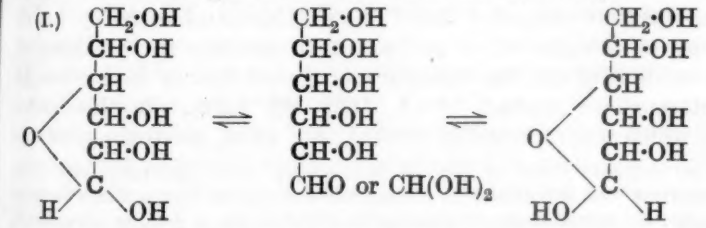
CLXXXVIII.—*Studies of Dynamic Isomerism. Part XVIII. The Mechanism of Mutarotation.**

By THOMAS MARTIN LOWRY.

1. *Mutarotation due to Isomeric Change.*

(*a*) The explanation that is now generally accepted of the mutarotation of the sugars is illustrated in the following scheme I.

(I.)



* This paper was read on Dec. 20th, 1923, as a verbal reply to the assertion made by Baker, Ingold, and Thorpe at a meeting on Nov. 15th, 1923, that water "does not intervene" in the mutarotation of the sugars. It has been held back for more than a year in order that the reply to their paper (J., 1924, **125**, 268), instead of being merely polemical in character, might be based on new experimental data. Although, therefore, the present paper contains a direct denial of their doctrine of non-intervention, its principal value is to serve as an introduction to a new series of experimental papers, of which the first is printed below.

This scheme, which was first put forward in 1903 by the author of the present paper, was developed in Prof. Armstrong's laboratory at South Kensington in three successive stages as follows:

(i) *The fundamental hypothesis*, that *mutarotation is due to reversible isomeric change*, was suggested for the first time in 1899 in a paper on "Nitrocamphor as an Example of Dynamic Isomerism" (Lowry, J., **75**, 211). Since the mutarotation of nitrocamphor could take place in a large range of organic solvents, and must therefore proceed without any change of composition, it was suggested that the mutarotation of the reducing sugars might be due to a similar *reversible isomeric change**, instead of to the *reversible hydration*, $C_6H_{12}O_6 + H_2O \rightleftharpoons C_6H_{14}O_7$, which E. Fischer (*Ber.*, 1890, **23**, 2326) had postulated on the basis of an analogy with the mutarotation caused by the reversible hydrolysis of gluconolactone, $C_6H_{10}O_6 + H_2O \rightleftharpoons C_6H_{12}O_7$.

(ii) The second step was the identification of the isomeric sugars as the parent compounds of the α- and β-glucosides; this was rendered probable by the observations of Simon in 1901 (*Compt. rend.*, **132**, 407), but was finally established by E. F. Armstrong in 1903 (J., **83**, 1305) by a direct process of hydrolysis by enzymes.

(iii) *The subsidiary hypothesis*, that *the isomeric change of the oxidic sugars proceeds through the intermediate formation of an aldehydic form of the sugar*, which completes the above scheme, was put forward in 1903 (Lowry, J., **83**, 1316) simultaneously with the publication of E. F. Armstrong's paper. This hypothesis was introduced in order to account for the fact that, although a direct interchange of H and OH appears to be impossible in the sugar series, the isomeric change established by Armstrong involves an inversion of sign of *one* of the four >CH·OH groups of the sugar. It was therefore suggested that "the simplest mechanism by which this can be brought about is that which involves the breaking of the γ-oxide ring and the formation of *the aldehyde or its hydrate* as an intermediate product" † (J., 1903, **83**, 1316). In this statement, which was repeated in 1904 (J., **85**, 1565), no distinction was

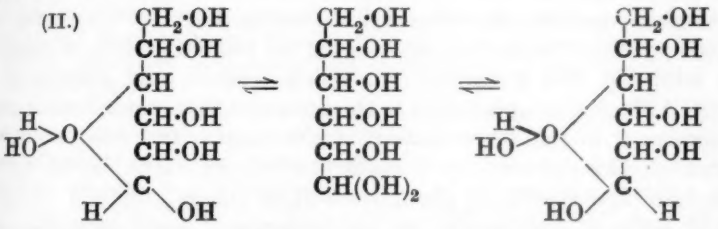
* Two isomeric forms of glucose had already been isolated; but their mutarotation was attributed to a complete conversion into a third form of the sugar, the equilibrium mixture being mistaken for a definite compound, just as in the analogous case of π-bromonitrocamphor, of which three forms had been described, one of them being an equilibrium mixture of the other two.

† Baker, Ingold, and Thorpe (J., 1924, **125**, 268) have adopted the former of these alternatives, but have attributed its origin to a German publication of later date. The latter alternative is attacked under the title of "Lowry's hypothesis." It is noteworthy that Kuhn and Jacob (*Z. physikal. Chem.*, 1924, **113**, 3195) have quoted the misleading version of my views given by Baker, Ingold, and Thorpe, which they have assumed to be correct, and have ignored my own published statements on the subject.

made between these two forms of the intermediate compound, since either would fulfil equally well the condition, on which the subsidiary hypothesis of an intermediate phase was based, that the optical inversion of the terminal carbon atom must proceed through an intermediate compound in which this atom is no longer asymmetric.

(*b*) The mechanism by which the intermediate aldehydic sugar is formed was discussed in 1904 (J., **85**, 1567), when it was shown that the hydrate, which is the first product of the action of aqueous alcohol on α-glucose, exhibits just the same mutarotation as α-glucose itself,* and cannot therefore be (as Hudson subsequently suggested, *J. Amer. Chem. Soc.*, 1909, **31**, 67) the intermediate aldehydrol. An equation was therefore given in which the interconversion of α- and β-glucose in presence of water was represented as depending on a double isomeric change, the two glucoses as well as the intermediate aldehyde being shown as hydrates, as in the following scheme II :

(II.)



The " reversible hydrolysis " referred to in 1903 (J., **83**, 1320) as a possible explanation of the catalysis of glucose by neutral water (in contrast with the inability of chloroform to catalyse the mutarotation of nitrocamphor) and the " hydrocatalysis " referred to in 1904 (J., **85**, 1658) must therefore both be interpreted as *an isomeric change consequent upon the addition of water*, since the initial act of hydration is too rapid to produce a mutarotation which can be followed experimentally.†

Before passing away from Scheme II above, it is important to notice that, although other substances may promote isomeric change by forming addition compounds in the manner there suggested, water is unique in that it is the only simple substance which can be

* Compare Riiber, *Ber.*, 1922, **55**, 3132; 1923, **56**, 3185.

† The " hydrate theory " which is attacked by Baker, Ingold, and Thorpe under the designation of " Lowry's hypothesis " is therefore not the one which I developed and described in 1904, but a modification of it which is actually incompatible with my own experimental work, since they assume throughout that the initial process of hydration is the direct cause of the observed changes of rotation, whereas I showed 20 years ago that the initial act of hydration is too rapid to be detected in this way.

added to the aldehydic group of a sugar without destroying its symmetry. In any other type of addition but that represented by the general equation $C_6H_{12}O_6 + R_2O = C_6H_{12}O_5(OR)_2$ the asymmetric character of the terminal carbon atom would be perpetuated, and could only be destroyed by shaking off the catalyst and liberating the free aldehyde, or alternatively by replacing the catalyst by a molecular proportion of water.

(*c*) In the later editions of Meyer and Jacobson's "Lehrbuch der organischen Chemie," Jacobson and Stelzner cite the aldehydic mechanism, which I put forward in 1903, as an example of a generalised phenomenon which they call "oxo-cyclo-desmotropy." The term desmotropy, which was introduced by Jacobson (*Ber.*, 1887, **20**, 1732; 1888, **21**, 2628) to describe "a rearrangement of bonds consequent upon the displacement of a hydrogen atom," does not here refer (as in the usage suggested by Hantzsch and Hermann) to the possibility of isolating either α- and β-glucose or the intermediate aldehydic form of the sugar, but only to the fact that these isomerides can be transformed into one another by displacing a single hydrogen atom and rearranging the related system of bonds. In adopting this generalisation, Baker, Ingold, and Thorpe (J., 1924, **125**, 268) coupled with it the assertion that water "does not intervene" in the mutarotation of the sugars, and attempted to establish this doctrine by a mathematical argument, based upon the form and spacing of the mutarotation curves, followed by two short series of experiments on the influence of small quantities of added water on the velocity of mutarotation of glucose in methyl alcohol and of tetra-acetylglucose in ethyl acetate. Although these experiments were put forward as "crucial" tests in support of their doctrine of non-intervention, the results are all compatible with a hydrate-mechanism in a system containing (i) sugar, (ii) water, (iii) a hygroscopic solvent, (iv) an unknown catalyst;* they can therefore only be regarded as inconclusive.† There is,

* By working under "clean" conditions, Mr. Owen has been able to arrest completely during a period of 24 hours the mutarotation of a solution of tetra-acetylglucose in ethyl acetate; the mutarotation observed by Baker, Ingold, and Thorpe in dry ethyl acetate was therefore due entirely to catalysis by unknown impurities in their solutions.

† The mathematical calculations for a two-component system are invalid when applied to a three-component system in which the active mass of the water is not the same as its total concentration. This identity might perhaps be assumed in the case of an "ideal" solution, conforming rigidly to Raoult's law of vapour-pressure lowering; but no "ideal solution" is known in which water is one of the components. The presence of a fourth component of unknown origin, character and concentration is even more incompatible with the essential conditions for a crucial test, since if an auxiliary catalyst is necessary, in order to establish the existence of a particular type of curve,

indeed (as in 1904, J., 85, 1566), no valid evidence in the literature to prove that mutarotation can take place except by the intervention of water; * and, since water is known to form a hydrate with the sugar, it would be absurd to suggest that this particular catalyst acts from a distance instead of acting in the normal way by entering into combination with the substance catalysed. In this connexion it is noteworthy that the mutarotation of beryllium benzoylcamphor (which is insoluble in water and forms no hydrates with it, but gives a crystalline addition compound with chloroform) is catalysed by chloroform, although this solvent has been found to inhibit the mutarotation of nitrocamphor, of β-bromonitrocamphor and of tetramethylglucose. This is not likely to be a mere coincidence, and therefore provides strong confirmation of the generally accepted view that one essential property of a catalyst is that it must be able to add on to and split off from the substance catalysed.†

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it should obviously have been added deliberately to materials of which the purity had been established by observing an arrest of mutarotation, instead of being introduced in the form of a casual impurity from the apparatus, solvent or sugar.

In addition to limiting their calculations to two out of four components of the systems studied, the authors impose a drastic limit to the range of concentrations within which they regard it as legitimate to test their doctrine of non-intervention experimentally. Thus, in seeking to prove that the velocity of mutarotation, k, is independent of the concentration, b, of added water, the total concentration of water must not be *too large*, since it is obvious that large additions of water produce large accelerations; and it must not be *too small*, since in the region covered by the phrase "Bakerian dryness" the accelerations produced by traces of water are assumed to be enormous in comparison with their concentrations. There is, however, supposed to be a minute intermediate region, lying below 0·1% of water, in which $dk/db = 0$. The existence of a small "flat" of this kind on the velocity–concentration curve is quite compatible with a hydrate mechanism in a four-component system, which could even give rise to a minimum; but if the experiments quoted as evidence of its existence are examined in the light of the data given in Part XIX below, it will be seen that dk is negligible merely because db also is negligible, and that the "crucial test" is therefore not far removed from the familiar fallacy of supposing that the ratio of two negligible quantities must also be negligible. There is, in fact, with the possible exception of the hitherto unexplored region of Bakerian dryness and purity, no range of concentrations in which the calculated acceleration for 0·1% of water (corresponding with a half-change period of about 3 months) could be detected with certainty by the methods now in use for measuring the velocities of mutarotation.

* The question of alternative catalysts, acting in the same way as water but not containing water, will be discussed fully in a subsequent paper.

† The modern view of the action of catalysts may be summed up by saying that "A catalyst is a reagent which is reproduced as one of the products of the reaction."

2. *Mutarotation dependent on the Intervention of a Catalyst.*

Although attempts to establish the mechanism of chemical changes by dynamical arguments are generally futile (as in the case of hydrolysis, where no conclusive proof has emerged after 50 years of experiment), it is of interest to notice the conclusions to which such arguments lead when viewed in the light of the admissions which were made during the discussion on the present paper, namely (i) that the mutarotation of the sugars in all solvents is dependent on the presence of water, and can be stopped by the removal of water, (ii) that the arrest of mutarotation by drying is easy, and does not require a condition of "Bakerian dryness."

(*a*) If we represent a "tautomeric mechanism," in which water plays no essential part, by the scheme IV,

$$\text{(IV.)} \qquad S_\alpha \rightleftharpoons A \rightleftharpoons S_\beta$$

where S_α and S_β represent α- and β-glucose and A is the intermediate aldehyde, we must represent the "hydrate mechanism" which I suggested in 1904 by a similar abbreviation of scheme II above, as follows :

$$\text{(V.)} \qquad S_\alpha{\cdot}H_2O \rightleftharpoons A{\cdot}H_2O \rightleftharpoons S_\beta{\cdot}H_2O.$$

It is then clear that no dynamical analysis can distinguish between the *form* of the mutarotation curves corresponding to schemes IV and V, since in both cases the mutarotation is attributed to two successive isomeric changes.

(*b*) As regards the *spacing* of the curves (*i.e.*, the rate of variation of the velocity of change with the concentration of added water), it is, however, possible to make a comparison of some value between schemes IV and V. Since the hydration of each form of the sugar is a reversible process, the two schemes must be shown in parallel, thus

$$\text{(VI.)} \qquad \begin{array}{ccccc} S_\alpha & \rightleftharpoons & A & \rightleftharpoons & S_\beta \\ \Downarrow\Uparrow & & \Downarrow\Uparrow & & \Downarrow\Uparrow \\ S_\alpha{\cdot}H_2O & \rightleftharpoons & A{\cdot}H_2O & \rightleftharpoons & S_\beta{\cdot}H_2O \end{array}$$

Moreover, since hydration is very rapid, the vertical arrows must be regarded as representing changes which are reversible, but which in practice are almost instantaneous. The proportion of the sugar which is hydrated, as in the lower line of this scheme, can be reduced to zero by careful drying; but it is not certain that it can be increased to 100%, since in the analogous case of gluconic acid the compound becomes partly dehydrated by forming a lactone even in dilute aqueous solutions. We can, however, compare the efficiency of the two mechanisms by noticing the velocity of change (i) in the absence of water, when only the "tautomeric mechanism" is available, and (ii) in aqueous solutions, when the "hydrate

mechanism " is at its maximum efficiency, although still working in parallel with the " tautomeric mechanism," since this cannot be inhibited completely by adding water. Experiments on these lines show at once that, in the absence of the " hydrate mechanism," the " tautomeric mechanism " produces no " flow " at all from S_α to S_β, whilst quite a rapid flow is produced whenever the " hydrate mechanism " is available. If, therefore, the question is to be settled by tests of this kind, we must conclude that *the direct interconversion of the anhydrous sugars indicated by the dotted arrows does not in fact take place* and that the only channel which is open from S_α to S_β is the one that passes through $S_\alpha \cdot H_2O$, $A \cdot H_2O$ and $S_\beta \cdot H_2O$.*

(*c*) It is interesting in this connexion to consider the behaviour of substances in which the asymmetry of the terminal carbon atom would be retained in the intermediate addition compound, as in the alcoholate of an aldehydic sugar, $-CH<^{OR}_{OH}$, or the hydrate of an anilino-sugar, $-CH<^{OH}_{NHPh}$. In all such cases the intermediate compound would exist in two forms, which we can call $A_\alpha \cdot H_2O$ and $A_\beta \cdot H_2O$; and, since these can revert only to S_α or to S_β respectively, the channel from S_α to S_β through $A \cdot H_2O$ is now blocked. Since, however, $A_\alpha \cdot H_2O$ and $A_\beta \cdot H_2O$ are dissociable compounds, inversion can still occur by dissociation to the " symmetrical " compound A, as in scheme VII :

(VII.) $$A_\alpha \cdot H_2O \rightleftharpoons A + H_2O \rightleftharpoons A_\beta \cdot H_2O.$$

All the arrows shown in the principal scheme VI (except the dotted arrows of the inoperative " tautomeric " mechanism) now represent essential stages in the process, since the whole of the material must now pass through A, as well as through $A \cdot H_2O$ which provides the sole means of access to A; but, if the reversible hydration of the compound A is rapid, the " flow " need not be greatly retarded by this additional stage in the process. The fact that an anilino-sugar can undergo change only through an anhydrous form of the open-chain compound does not therefore eliminate the necessity for the formation of a hydrate (or of some analogous intermediate addition compound) unless we are to suppose that the isomeric changes of these compounds, unlike those of the parent sugars, do not depend on the presence of water.†

* The possibility of an alternative catalyst acting in the same way as water is again reserved for consideration at a later stage.

† Since the anilino-sugars are stable in presence of alkalis, it is possible that there may be a fundamental difference in the mechanism of the isomeric changes which they undergo, but only in presence of acid catalysts; the experimental data are, however, too scanty for a useful discussion at the present stage.

(*d*) It will be seen that whilst in 1904 I laid stress on the experimental fact of the formation of hydrates by the mutarotating sugars of which glucose is the type, Jacobson lays stress on the presence of a mobile hydrogen atom in these sugars. It is possible, however, in the light of modern theories of valency, to see that these ideas are not incompatible. Thus, the hydrolysis of an ester was formerly regarded as depending on the formation of an addition compound of the ester with water and the catalyst, thus :

$$[\text{Ester, NaOH, } H_2O] \text{ or } [\text{Ester, HCl, } H_2O].$$

At the present time, however, we should regard the metal in the addition compound as ionised, and assert that it is only the hydroxyl ion of the alkali and not the whole molecule that is really added to the ester; and in a similar way that it is only the hydrogen ion and not the whole molecule of the acid that is added, thus :

$$[\text{Ester, OH, } H_2O]^-Na^+ \text{ or } [\text{Ester, H, } H_2O]^+Cl^-.$$

The same treatment can, however, also be applied to the water in this scheme, which provides a hydrogen ion to supplement the hydroxyl ion of the alkali, or a hydroxyl ion to supplement the hydrogen ion of the acid, thus :

$$\left[\text{Ester, OH, H}\right]^{Na^+}_{OH^-} \text{ or } \left[\text{Ester, H, OH}\right]^{Cl^-}_{H^+}.$$

The brackets now contain just the elements that are needed to form the ultimate products of hydrolysis, whilst the ions of the catalyst outside the bracket can be set free to act upon another molecule of the ester.

In precisely the same way, the difference between my hydrate mechanism and Jacobson's desmotropic mechanism appears to depend on nothing more fundamental than the difference between the old view, represented by the equation $NH_3 + HCl = NH_4Cl$, in which the union of ammonia and hydrogen chloride is represented as the formation of an addition compound, and the newer view which regards it as involving only the transfer of a proton from the acid to the base :

$$NH_3 + HCl = \overset{+}{N}H_4 + \overset{-}{Cl}.$$

Thus on general grounds we might consider that the mutarotation of an aqueous solution of a sugar in presence of an acid or basic catalyst must involve the formation of an intermediate addition compound of the sugar with the other compounds, thus :

$$[\text{Sugar, } NH_3, H_2O] \text{ or } [\text{Sugar, HCl, } H_2O].$$

If, however, we adopt the more modern method of formulation, and regard the acid as a proton donator and the base as a proton acceptor, and attribute to the water (as in hydrolysis) a converse

function to that of the catalyst with which it is associated, we can rewrite the schemes which represent the addition of the catalysts to the sugar in such a way as to show only the transference of a proton which is the essential feature of Jacobson's process of desmotropy, thus :

$$\left[\text{Sugar}, \; -\text{H}, \; +\text{H}\right]^{\text{NH}_4^+}_{\text{OH}^-} \quad \text{or} \quad \left[\text{Sugar}, \; +\text{H}, \; -\text{H}\right]^{\text{Cl}^-}_{\text{H}^+}.$$

The remainder of this paper is therefore based on the assumption that, since a catalyst is needed in all desmotropic changes, there need be no controversy in reference to the special case of desmotropic change which gives rise to the mutarotation of the sugars. I have therefore worked out, on the basis of the analogy with hydrolysis which is outlined above, a detailed mechanism for the isomeric change of the sugars, and of prototropic compounds generally, on the lines foreshadowed in 1904, but in such a way as also (i) to indicate the important part played by the mobile hydrogen atom, and (ii) to assign a definite function, not only to water, but also to acids and bases, when acting as catalysts for the mutarotation. This detailed mechanism is perhaps incapable of rigid proof, and no crucial tests of its correctness are offered, but it certainly possesses the attributes by which Pasteur claimed to recognise a " true " theory, since it has enabled us to foresee the possibility of a number of important phenomena, which would otherwise have been quite unexpected, but which have since been verified experimentally.

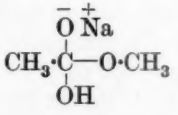
3. *The Mechanism of Hydrolysis and Esterification.*

On the experimental side, the mutarotation of nitrocamphor and of the sugars shows certain points of resemblance (which it would be unwise to overlook) to the hydrolysis of an ester. Thus, whilst the inversion of sucrose and the hydrolysis of a glucoside are commonly effected with the help of enzymes or of acids, the mutarotation of the reducing sugars, like the hydrolysis of an ester, is accelerated both by acids and by alkalis. Moreover, just as in hydrolysis, alkalis are in general more efficient catalysts than acids. For this reason, the view has been advanced that the reducing sugars are amphoteric, like the esters, the dissociation constant of the sugar as an acid ($K_a = 10{\cdot}5 \times 10^{-13}$ for glucose at 25°) * being much larger than its dissociation constant as a base ($K_b = 7{\cdot}8 \times 10^{-17}$ at 25°; Kuhn and Jacob, *Z. physikal. Chem.*, 1924, **113**, 395).

The intermediate compounds formed by combination with acidic and basic catalysts do not appear to have been isolated in the case of the reducing sugars, with the exception of certain com-

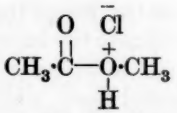
* Euler, Myrbäch, and Rudberg (*Arkiv Kemi, Min. Geol.*, 1923, **8**, No. 28) give $K_a = 0{\cdot}12, \; 0{\cdot}31, \; 0{\cdot}71 \times 10^{-14}$ at 0°, 10°, and 20°.

pounds of the aldehyde-ammonia type;* but in the case of the esters, where a larger range of materials is available, this has been done in certain instances. Thus an addition compound of sodium methoxide with ethyl benzoate has been isolated by von Pechmann (*Ber.*, 1898, **31**, 503); and an unstable addition compound of ethyl acetate with hydrogen bromide, m. p. — 36°, has been isolated by Maass and McIntosh (*J. Amer. Chem. Soc.*, 1912, **34**, 1272). The electronic theory of valency requires, however, that all these addition compounds must be formulated as "salts," held together by the electrostatic attraction of oppositely charged ions and not by real bonds, since any process of electron sharing would at once create a surplus of electrons. The initial addition compounds of methyl acetate with sodium hydroxide and with hydrogen chloride may therefore be written as follows:



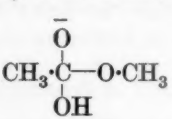
Oxy-salt.

and

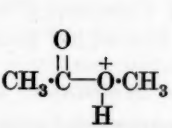


Oxonium salt.

If the free ions are omitted, the complexes formed by the combination of the ester with the hydroxyl or hydrogen ion of the catalyst may be formulated as follows:

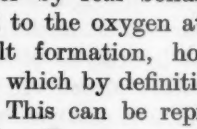


and

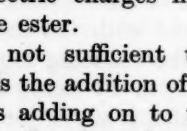


In these complexes hydroxyl and hydrogen, supplied by the catalyst in the form of ions, are now represented as neutral radicals, joined to the ester by real bonds, their electric charges having been transferred to the oxygen atoms of the ester.

Mere salt formation, however, is not sufficient to produce hydrolysis, which by definition demands the addition of a molecule of water. This can be represented as adding on to the oxygen atom which still remains unoccupied in the above formulæ, thus:

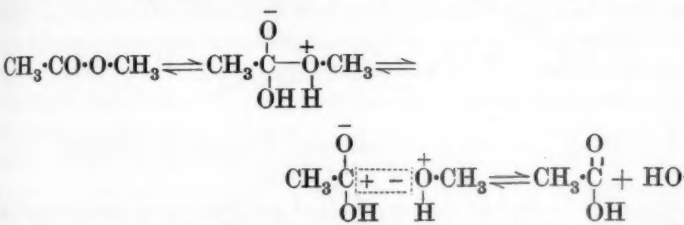


and



* Lobry de Bruyn, *Rec. trav. chim.*, 1893, **12**, 286; 1895, **14**, 134; 1899, **18**, 72; Ling, J., 1922, **121**, 1384; *J. Soc. Chem. Ind.*, 1922, **41**, 151. Compare also the addition compounds with guanidine (Morrell and Bellars, J., 1907, **91**, 1010).

If the free ions associated with the complex are again neglected, it will be seen (i) that the hydrolysis of an ester both by alkaline and by acid catalysts proceeds by the addition to the ester of hydrogen and hydroxyl radicals which are supplied to it in the form of ions; (ii) that whilst one of these ions is derived from the catalyst, the water provides either hydrogen ions to supplement the hydroxyl ions of an alkaline catalyst, or hydroxyl ions to supplement the hydrogen ions of an acid catalyst, and (iii) that this addition gives rise in each case to the same bipolar molecule (or "Zwitterion"), which is shown as an intermediate product in the following scheme:

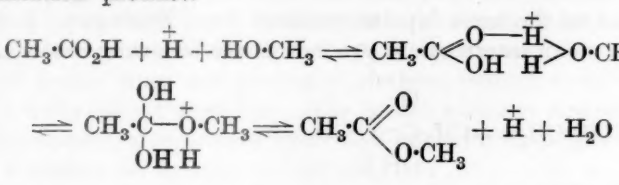


In this scheme, the hydrolysis of an ester is formulated, like the hydrocatalysis of glucose, as an "isomeric change following the addition of water"; but the "isomeric change" now takes the form of a fission of the molecule by the rupture of a bond, the final ionisation of which provides the electric charges which are needed to neutralise those already present in the "Zwitterion."

The reverse process of esterification, which is of interest in connexion with the reconversion of the aldehydic form of a sugar into the stereoisomeric oxides, only takes place in presence of *acid* catalysts. It may be formulated in a converse way as depending on the formation of an addition compound of the acid and alcohol with the catalyst, followed by the removal of a molecule of water and the liberation of the catalyst from the complex. The condensation of the alcohol and acid therefore appears to involve (i) the repression of the ionisation of the organic *acid*, with a development of its ketonic functions (J., 1923, **123**, 827), (ii) the addition of a proton to the *alcohol* (compare Goldschmidt and Udny, *Z. physikal. Chem.*, 1907, **60**, 728), thereby giving to the alcohol the proton-donating functions of an acid,*

* Compare the view that aqueous acids are really oxonium salts, containing oxonium ions and not free protons, the separation of which has been formulated as an endothermic action involving the absorption of 262,000 calories (Fajans, *Ber. phys. Ges.*, 1919, **21**, 709). If this estimate is even approximately correct, it is evident that, not only must the ionisation of an acid be formulated as a double decomposition, $H_2O + HCl \rightleftharpoons \overset{+}{H_3}O + \overset{-}{Cl}$, and not as a dissociation, $HCl \rightleftharpoons \overset{+}{H} + \overset{-}{Cl}$, but that physical chemists have made

(iii) the co-ordination of the proton of this complex with the carbonyl oxygen of the acid (compare Pfeiffer, *Annalen*, 1913, **398**, 152) as a preliminary to (iv) the addition of the proton-donating complex of the alcohol to the carbonyl group of the acid, according to the normal rules for the addition of a hydride such as HCN to an aldehyde or ketone, (v) the elimination of the proton of the catalyst, and of a molecule of water, from the intermediate condensation product.



4. *Prototropy* as an Intermolecular Process of Addition and Removal of a Proton.*

The fact that water as well as alkali or acid is needed for hydrolysis scarcely needs demonstrating, but when dealing with isomeric changes the function of water as a promoter of chemical action is less obvious. Here again, however, just as in the case of hydrolysis, there is an instructive contrast between two principal groups of cases, since the *ionotropic changes* of the aromatic series, *e.g.*, $C_6H_5\cdot NHCl \longrightarrow C_6H_4Cl\cdot NH_2$, which involve the migration of other ions as well as of a proton, are catalysed only by acids, like the inversion of sucrose, whilst *prototropic changes*, which involve only the migration of a proton, are catalysed both by acids and by alkalis, like the hydrolysis of an ester.

It must, however, be remembered that prototropic change cannot be regarded as a mere jumping of a proton from one point to another *within the molecule*, as in the old theory of tautomerism, but must be represented as an intermolecular action, which depends (like so

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a mistake in formulating the ionisation of water as $H_2O \rightleftharpoons \overset{+}{H} + \overset{-}{O}H$, since this action also should be regarded as a transfer of protons, $2H_2O \rightleftharpoons H_3\overset{+}{O} + \overset{-}{O}H$ (compare the redistribution of protons in the balanced action $CO_2 + 2NH_3 \rightleftharpoons NH_2\cdot CO\cdot O\cdot NH_4$) instead of as a simple dissociation into hydrogen and hydroxyl ions.

* It has been suggested that the transfer of a proton would be described more accurately as "protonotropy." In the present paper the shorter form suggested in 1923 (J., **123**, 828) has been retained provisionally, on the ground that the "n" of the word proton, although convenient as a mnemonic, is not essential to the definition. The longer form is, however, attractive on account of its more fully descriptive character, and might be allowed to take the place of the shorter form if it should prove in practice to be more acceptable.

many other chemical changes *) on the presence of molecules of other kinds, and may therefore be suspended if these are not present in the system. In particular, all prototropic changes appear to involve two distinct † chemical processes, as follows: (i) the removal of a proton from one part of a molecule to some outside basic or proton-accepting component of the system, and (ii) the addition to another part of the molecule of a proton, also derived from outside, namely, from some acidic or proton-donating component of the system. Moreover, a base which is very efficient in removing a proton from the organic molecule will be correspondingly reluctant to part with the proton that is required to reconvert the organic ion into a neutral molecule; and an acid which is ready to supply a proton to the organic ion will tend to repress the equally essential removal of a proton from the organic molecule. Whilst, therefore, prototropic changes are catalysed both by acids and by bases, we might anticipate that a base would be most efficient when water is also present to act (like a weak acid) as a source of protons for the organic ion, and in the same way that an acid might be most efficient when water is added to act (like a weak base) as an acceptor of protons from the isomeric hydrides. The experimental verification of this prediction, which follows naturally from the mechanism described above (but which could certainly not be deduced from the dictum that "the mode of action of catalysts is quite unknown") is summarised in Part XIX below; but it is also being used as a basis for the further extended investigation which the importance of the observations demands.

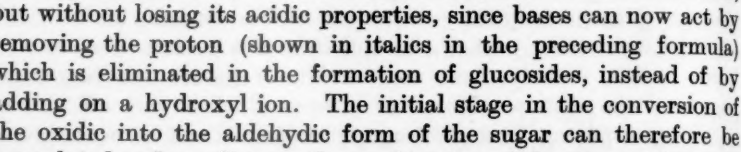
5. *Mechanism of Isomeric Change in the Reducing Sugars.*

The chemical changes involved in the interconversion of α- and β-glucose through the intermediate formation of the aldehydic form of the sugar are intermediate in character between those described in §§ 3 and 4 above, since (i) *the breaking of the ring in the oxidic sugars involves the rupture of a carbon–oxygen bond*, just as in the hydrolysis of an ester or of Fischer's mutarotating gluconolactone, but (ii) *the formation of the aldehyde is not accompanied by a change of composition*, so that, even when the change is determined by the action of water, this action must be classed as a hydrocatalysis and not as a simple hydrolysis. Further investigation shows, however, a very close analogy between the hydrolysis of gluconolactone and the hydrocatalysis of glucose. Thus, on the

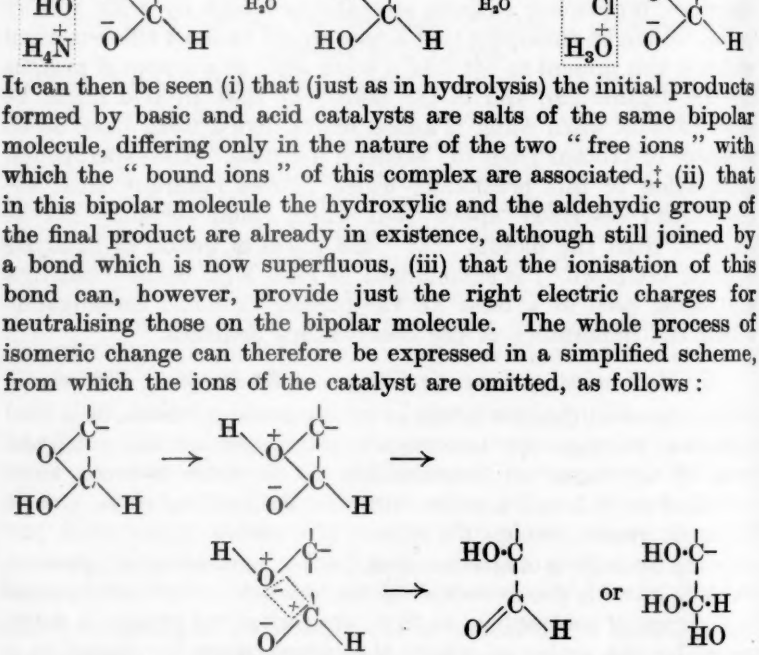
* It is probable that the only real intramolecular changes are those of the radioactive type, in which *even the other atoms in the same molecule* do not intervene to accelerate or retard the action.

† These changes may, however, occur simultaneously in the same electric circuit, as in Armstrong's electrolytic theory of chemical change.

one hand, the same basic C–O–C group is available in both compounds to provide a point of attachment for acid catalysts or for water. On the other hand, the carbonyl group, which forms the natural point of attachment for bases, both in the case of the esters and of gluconolactone, has now been reduced, $>C{=}O \rightleftharpoons >CH{\cdot}O\mathit{H}$, but without losing its acidic properties, since bases can now act by removing the proton (shown in italics in the preceding formula) which is eliminated in the formation of glucosides, instead of by adding on a hydroxyl ion. The initial stage in the conversion of the oxidic into the aldehydic form of the sugar can therefore be formulated as depending on the combination of the sugar either with *base plus water* or with *acid plus water* * as in the following scheme: †



It can then be seen (i) that (just as in hydrolysis) the initial products formed by basic and acid catalysts are salts of the same bipolar molecule, differing only in the nature of the two "free ions" with which the "bound ions" of this complex are associated,‡ (ii) that in this bipolar molecule the hydroxylic and the aldehydic group of the final product are already in existence, although still joined by a bond which is now superfluous, (iii) that the ionisation of this bond can, however, provide just the right electric charges for neutralising those on the bipolar molecule. The whole process of isomeric change can therefore be expressed in a simplified scheme, from which the ions of the catalyst are omitted, as follows:



* The question of mutarotation in isoelectric solutions will be discussed in a later paper.

† In this scheme, the intermediate atoms of carbon in the γ-oxide ring are omitted.

‡ The bipolar molecule can scarcely be expected to exist except in the form of a salt (or of a hydrate if water plays the part of the acid and base). The extent to which it is formed, and the velocity of the chemical changes in which it is concerned, will therefore depend on the strength of the acid or base with which it is combined.

In the final stage of this scheme both of the alternative products are shown, namely, the *aldehyde*, which is produced if the electric charges of the ionised carbonyl group are neutralised by forming a double bond, and the *hydrate*, which is produced when these charges are neutralised by adding on the ions of water.

6. *Conclusions.*

The mechanism set out in § 5 above is put forward as a natural development, in view of the clearer conceptions of the electronic theory of valency, (i) of the fundamental hypothesis (J., 1899, **75**, 213) that the mutarotation of the sugars is due to a reversible isomeric change, and (ii) of the subsidiary hypothesis (J., 1903, **83**, 1316) that this change proceeds through an intermediate aldehydic phase; it also embodies (iii) E. F. Armstrong's "oxonium" formula for the hydrate of α-glucose (J., 1903, **83**, 1309) and (iv) the formulation of hydrolysis as an isomeric change following the addition of water (J., 1904, **85**, 1567). It appears to cover all the essential points raised by Baker, Ingold, and Thorpe, but goes beyond the point that was reached in our 1899 or in their 1924 paper, in that it not merely attributes mutarotation to isomeric change, but also assigns a definite part to those chemical agents without which, it appears, mutarotation cannot proceed. In this way, it removes some of the vagueness which attaches to the use of the terms "tautomerism" and "catalysis" in connexion with the phenomena of mutarotation, since these terms have served hitherto mainly as a cloak to conceal our ignorance of the method of action of these essential chemical agents, although their importance has long been obvious.

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CAMBRIDGE. [*Received, March 4th*, 1925.]

CLXXXIX.—*Studies of Dynamic Isomerism. Part XIX. Experiments on the Arrest of Mutarotation of Tetramethylglucose.*

By THOMAS MARTIN LOWRY and EVAN MATTHEW RICHARDS.

1. *Classification of Solvents.*

The mechanism described in Part XVIII (preceding paper) leads to the conclusion that it should be possible to divide solvents into three groups as regards their behaviour towards prototropic changes, such as those which give rise to the mutarotation of the sugars, thus:

(i) The first group should include all those solvents which can receive a proton from the compound or give a proton to its ion. These amphoteric solvents should act as *complete catalysts* for the mutarotation.

(ii) The second group should include solvents which possess either basic or acidic properties, but not both. Solvents of this group may be unable to act as complete catalysts when used alone, but may become very efficient when used as one component of a *mixed catalyst*.

(iii) The third group should include solvents which possess neither basic nor acidic properties, and which may therefore be expected to possess no catalytic properties for this particular type of isomeric change.

In the paper in which the mutarotation of nitrocamphor was first described, organic solvents were divided into two groups as follows.* "In solvents containing oxygen, such as the alcohols, acids, ethers and ethereal salts, equilibrium is reached on the average in about four hours at 15°. The hydrocarbons and compounds such as chloroform and carbon disulphide are much less active, and a period of from two days to a week or more is required before equilibrium is reached in these solvents" (J., 1899, **75**, 219). The view was also advanced that "From certain observations that have been made with chloroform solutions, it seems doubtful whether the second group of solvents are capable by themselves of bringing about the isomeric change at all." The occasional arrest of mutarotation in solutions of nitrocamphor in *chloroform* was, indeed, clear proof that the isomeric change was not spontaneous, and could not proceed in the absence of a catalyst; but it was not until 10 years later (J., 1908, **93**, 119) that the discovery of the anticatalytic action of carbonyl chloride made it possible to repeat the observation of arrested mutarotation in two other solvents, namely *benzene* and *ether*, and thus to eliminate them from the category of "complete catalysts" for the mutarotation of nitrocamphor. The experiments on ether showed, moreover, that the presence of oxygen in the molecule was not the criterion of a complete catalyst, a conclusion that was afterwards confirmed by the experiments of Irvine and Scott (J., 1913, **103**, 584), in which the mutarotation of one of the dimethylglucoses was "suspended" for about a fortnight in a solution in *acetone*. There can therefore be little doubt that the real criterion for catalytic activity must be the possession of acid or basic properties as suggested in Part XVIII. This view has already been made the

* The same classification was adopted four years later by Stobbe (*Annalen*, 1903, **326**, 347) in connexion with keto-enolic changes.

basis of several series of new experiments (some of which are described below) and these have in every case given results which are in harmony with the mechanism now under examination.

2. *Discussion of Experimental Results.*

In the present paper the evidence as to the conditions under which mutarotation can take place has been extended in two directions (i) by repeating with a suitable sugar the observations which led to the original discovery of arrested mutarotation in nitrocamphor, (ii) by examining a number of additional solvents in which arrested mutarotation had not been observed previously either with nitrocamphor or with a sugar. The sugar selected was tetramethylglucose, the mutarotation of which was recorded by Purdie and Irvine in 1904 (J., **85**, 1049). Whereas glucose has been found to be quite unsuitable for experiments which depend on the use of carefully purified materials, tetramethylglucose has proved to be an ideal sugar for the purpose. The different behaviour of the two sugars cannot be attributed to any difference in their reactivity, or to a greater sensitiveness of glucose to the influence of catalysts, since their velocities of mutarotation are almost identical, except in the case of the low velocities which are recorded when attempts are being made to arrest the mutarotation completely by careful purification. The difference is therefore probably due to the fact that glucose can be crystallised only from water or from water-soluble solvents, under conditions which permit (and generally favour) contamination with water-soluble impurities. Tetramethylglucose, on the other hand, crystallises excellently from solvents such as light petroleum,* which not only tend to separate water-soluble impurities from the sugar, but can themselves be dried and purified by the most drastic processes.

(*a*) *Benzene and Chloroform.* The experiments varied very greatly in difficulty. It was found that the mutarotation in

* The tetramethylglucose used by us had been crystallised from light petroleum, boiling below 40°. When heated quickly, it melted at 88° (Purdie and Irvine give 88—89°), but when heated slowly it began to melt at 80°; the latter temperature may therefore be taken as the "equilibrium temperature" (Lowry, J., 1899, **75**, 233), or the "natural freezing point" (Findlay, "Phase Rule," 1923, p. 158) of the equilibrium mixture. On the assumption that the dispersion ratio a_{5893}/a_{5461} has the usual value 0·85 of the sugar series, the rotatory powers may be compared with those given by Purdie and Irvine as follows :

	In benzene.	In water.
L and R : $[\alpha]_{5461}$	129° ⟶ 103°	117° ⟶ 95°
L and R : $[\alpha]_{5893}$	109° ⟶ 88°	100° ⟶ 81°
P and I : $[\alpha]_{5893}$	111° ⟶ 85°	102° ⟶ 83°

benzene was very difficult indeed to arrest, a result that is in accordance with the view expressed in an earlier paper (J., 1904, **85**, 1566) that "although the proportion of water . . . may be small, the whole of it is available for hydrolysis," whereas in hygroscopic solvents "the activity of the water is greatly lessened by combination with the solvent." Similar difficulties would no doubt have been experienced in the case of *chloroform*, but for the fact that some samples happen to contain the right amount of carbonyl chloride to serve as an anti-catalyst for the more active impurities in the solution; we were therefore able, although only on one occasion, to observe in this solvent a particularly long arrest of mutarotation, extending over a period of about 10 days.

(*b*) *Ethyl Acetate.* The experiments on *ethyl acetate* were of special interest in view of the fact that Baker, Ingold, and Thorpe (J., 1924, **125**, 268) recorded a finite velocity of mutarotation for solutions of tetra-acetylglucose in dry ethyl acetate. Our experiments showed, however, that the mutarotation of tetramethylglucose in this solvent could be arrested completely during a period of several hours, although nothing of the sort was observed when glucose was used instead of the methylated sugar. Moreover, a preliminary experiment with a small sample of tetra-acetylglucose gave (with the help of a new technique) an exceptionally perfect arrest, during a period of about 24 hours. There can therefore be no doubt that ethyl acetate is not a catalyst for the mutarotation of the sugars, and that the finite velocities of mutarotation hitherto recorded have been due to the use of impure materials or to accidental contamination of the solutions.

(*c*) *Water and the Alcohols.* No such conclusive evidence is available as yet in the case of the alcohols. Irvine and Hogg (J., 1914, **105**, 1390) record that "when special precautions are adopted to secure the absence of catalysts, the mutarotation of monomethylglucose in methyl alcohol is so slow that the transformation $\alpha \rightleftharpoons \beta$ remains practically suspended"; but their numerical data show that the mutarotation, although "exceedingly slow," was of the same order as in the experiments with tetramethylglucose which are described below. Baker, Ingold, and Thorpe also record a finite velocity of mutarotation for solutions of glucose in dry methyl alcohol. Since none of the attempts made hitherto to arrest the mutarotation of a simple sugar * in methyl alcohol has been completely successful, it is only possible to conclude that methyl alcohol *may* be a complete catalyst, in

* Irvine and Hogg's experiments on monomethylglucoseanilide, in which mutarotation was observed only in presence of acids, will be discussed in a later paper.

virtue of its weak amphoteric properties, but that its efficiency as a catalyst is not greater than 3% of that of water.

Ethyl alcohol gives the same kind of ambiguous results as methyl alcohol, so that at the present time *water* is the only solvent of which we can assert definitely that it can act as a complete catalyst for the mutarotation of the sugars. The original proof that the catalytic activity of water does not depend on acid or basic impurities in the solvent or sugar was given in the first paper of this series (J., 1903, **83**, 1314); but the later quantitative studies of Osaka (*Z. physikal. Chem.*, 1900, **35**, 661), Hudson (*J. Amer. Chem. Soc.*, 1907, **29**, 1572), Euler (*Biochem. Z.*, 1920, **107**, 150; *Arkiv. Kem., Min. Geol.*, 1923, **8**, No. 28), and Kuhn and Jacob (*Z. physikal. Chem.*, 1924, **113**, 389) have confirmed this early view by showing that whilst the velocity of mutarotation passes through a minimum at an isoelectric point in slightly acid solutions ($p_H = 5$), it is not reduced to zero. There is, however, no justification as yet for asserting that water is the *only* complete catalyst for mutarotation, since there is no reason why the search for alternative catalytic solvents should not meet with the same success as the search for other ionising solvents for use as alternatives to water in electrolysis.

(*d*) Apart from water and aqueous alcohols, the only common solvents in which glucose dissolves freely are formamide and pyridine. The mutarotation of glucose in pyridine was first observed by Behrend and Roth in 1904 (*Annalen*, **331**, 361). The mutarotation was rapid, passing to completion during the first night *at a temperature of* 0°; if, therefore, these observations had been available when the classification of solvents into two groups was first suggested, there can be little doubt that pyridine would have been included with the oxygenated compounds in the *active* group of solvents. This conclusion would also have appeared inevitable in view of the well-known catalytic activity of bases in the mutarotation of aqueous solutions of glucose (O'Sullivan and Thompson, J., 1890, **57**; compare J., 1903, **83**, 1314), as well as of nitrocamphor in non-aqueous solutions (J., 1899, **75**, 221; 1908, **93**, 107). The statement that glucose undergoes mutarotation in pyridine has indeed been accepted without question during a period of 20 years, and has been quoted as valid evidence, first against Fischer's theory of hydrolysis as the cause of mutarotation, and then against the theory of hydrocatalysis. It is now shown to rest on no valid foundation of fact, since the minute residual velocity of mutarotation which was exhibited by solutions of glucose in dry pyridine disappeared completely in the case of tetramethylglucose, which gave a well-marked period of induction before mutarotation began to take place. Pyridine is therefore

the first clearly defined example of a substance which has no catalytic properties of its own for the mutarotation of the sugars, but which becomes extremely efficient when used as one constituent of a mixed catalyst. The discovery of this new type of catalyst may be regarded as a decisive vindication of the mechanism by which alone the attempt to arrest the mutarotation of a sugar in presence of a base was rendered a plausible proposition.

3. *Chloroform à Solvent but not a Catalyst.*

In the first experiment, a 4% solution of tetramethylglucose in a "pure" chloroform prepared by the United Alkali Company gave a fairly rapid mutarotation from $a = 9{\cdot}07°$ (initial) to 8·51° (final) in a 2-dcm. tube, in spite of the fact that a silica polarimeter tube was used. In a second experiment, however, an "arrest" of mutarotation was observed by using a 4% solution of tetramethylglucose in medicinal chloroform (containing alcohol), which had been purified by shaking three times with sulphuric acid and distilled. The part of the solution which was transferred to the silica polarimeter tube gave the following readings:

Time (days)	1	2	3	4	5	6	7	8	9	10
a_{5461} =	9·06°	9·02°	9·02°	8·96°	8·96°	9·01°	9·01°	9·07°	9·07°	9·08°

The temperature of the tube was kept at 20° for the first 120 hours, but the circulation of water at this temperature was stopped during the nights following the fifth day, although all the readings were still taken at 20°. At the end of a week, a few drops of the solution were added to make up for leakage or evaporation; the rotatory power of the solution in the tube may therefore have been increased slightly as the result of a slow evaporation of the volatile solvent, but this would not be sufficient to account for the arrest of mutarotation, since of half a dozen attempts to produce this effect only one was successful. The rotatory power of the remainder of the solution, which had been kept in a glass flask in a thermostat at 20°, had fallen at the end of 13 days about halfway towards the usual final value, the reading corresponding to those given above being $a = 8{\cdot}74°$.

The arrest of isomeric change in chloroform cannot be attributed either to excessive purification or to intensive drying. In particular, since the polarimeter tube could not be ignited, and was only dried by drawing air through it whilst still warm from prolonged steaming, the arrest of mutarotation could not be due to any approach to Bakerian dryness; moreover, minute traces of water were actually added on the eighth and ninth days, without initiating any rapid change. Traces of carbonyl chloride would, however,

not only remove bases in the form of carbamides, but would also replace small amounts of water by anhydrous hydrogen chloride, a compound which does not behave as an acid, and is probably not a catalyst, when water is not present (compare Soper, J., 1924, **125**, 768). In the same way, the addition of a drop of pyridine at the end of 10 days did not produce any immediate mutarotation, probably because, in the absence of water, the catalytic properties of this compound also are insignificant; but the addition of pyridine caused the solution to become cloudy and the observations were therefore discontinued.

4. *Experiments with Benzene.*

In the case of nitrocamphor it was shown in 1908 (J., **93**, 119) that, by working in silica vessels and in presence of traces of carbonyl chloride, the velocity of mutarotation in benzene could be reduced in the ratio of 125 : 1, from 0·0001 to 0·0000008, whilst the velocity in ether was reduced in the ratio of 50 : 1 from 0·0015 to 0·000026. The view was therefore expressed that "there can be little doubt that in ether, as in benzene and chloroform, the isomeric change is not spontaneous, but depends on the presence of impurities." No fresh experiments have been made in order to determine the behaviour of *ether* towards the sugars, but a new series of experiments has been made with solutions of tetramethylglucose in *benzene* as follows: (i) Commercial benzene was shaken repeatedly with sulphuric acid to remove thiophen, washed with aqueous sodium carbonate, dried over calcium chloride, frozen and drained until its freezing point was constant, stored for 18 months over sodium wire, distilled from phosphoric oxide in a glass flask which had been filled with concentrated sulphuric acid during a period of 6 months, and was finally collected (without using a condenser) in a silica flask cooled in ice covered with liquid paraffin. In spite (or because) of this careful purification, and of the fact that the solution was made up in a silica flask, and examined in a well-steamed silica tube, the mutarotation in *dry* benzene was complete within about 2 days, the period of half-change being 14 hours, and the velocity coefficient about 0·00086. In *wet* benzene, which had stood over water for 3 months, the mutarotation during the first day was about twice as fast as in dry benzene, with a velocity coefficient of 0·0016; but during the night the action proceeded more slowly, although the pump attached to the thermostat was left working, with the result that the average velocity was rather less than in the experiment with dry benzene. It therefore appeared possible that prolonged contact with water, by extracting water-soluble impurities from the benzene, had dimin-

ished its catalytic properties to approximately the same extent as prolonged drying by contact with sodium.

(ii) The attempt to clean the polarimeter tube by steaming was then suspended, since the tube appeared to be purified more effectively by repeated use with clean solvents. The silica tube with the best record was, therefore, merely rinsed with dry benzene, without even removing the end-plates. As a result, the velocity coefficient of a sample of tetramethylglucose, which had been dried by standing over sulphuric acid in a vacuum for 4 days, fell to one-eighth of the value formerly recorded, as is shown in Table I.

TABLE I.

Mutarotation of Tetramethylglucose in Dry Benzene.

(4% Solution by volume made up in a silica bottle, and examined in a 2-dcm. silica polarimeter tube at 20°.)

Time.	a_{5461}.	$k \times 10^3$.*	Time.	a_{5461}.	$k \times 10^3$.
12 mins.	10·32		7 days	9·08°	0·09
24 ,,	10·32		8 ,,	9·02	0·09
3 hours	10·33		9 ,,	8·93	0·09
18½ ,,	10·09	0·10	11 ,,	8·82	0·08
26½ ,,	10·00	0·11	13 ,,	8·79	0·07
46½ ,,	9·81	0·11			
54½ ,,	9·68	0·11	‡307 hours	8·79	
65½ ,,	9·57	0·11	308½ ,,	8·35	18
90½ ,,	9·44	0·10	309 ,,	8·33	17
98 ,,	9·40	0·10	310 ,,	8·30	
114½ ,,	9·29	0·10	311½ ,,	8·26	
122 ,,	9·25	0·10	314 ,,	8·26	8·26
138½ ,,	9·18	0·10	317½ ,,	8·28	
†147 ,,	9·14	0·10	330 ,,	8·24	

$k = 0{\cdot}00010$. Half-change period (obs.) = 114 hours.

* $k = 1/t \,.\, \{\log (a_0 - a_\infty) - \log (a_t - a_\infty)\}$. In calculating this coefficient the time was always expressed in *minutes*.

† At this stage the circulating water was stopped during the night-time, so that the average temperature of mutarotation was below 20°, although all the rotatory powers were read at this temperature.

‡ At 307 hours a trace of water was added to the solution in the tube; and from this time to the end the circulation of water at 20° was maintained continuously.

During the first 6 days the velocity coefficient was very steady at 0·0010, corresponding to a half-change period of 114 hours; after that, the circulation of water from the thermostat was maintained only during the day, and the velocity coefficient was therefore diminished slightly as a result of cooling during the night. After 13 days, a drop of water was added and the temperature was then maintained at 20° until mutarotation was complete. In this case *the addition of water increased the velocity of mutarotation more than* 100-*fold*. This result was in striking contrast to the failure of a much smaller quantity of added water to initiate a rapid

mutarotation in a solution of the same sugar in chloroform. The difference may be accounted for in part by the protective influence of carbonyl chloride in the chloroform; but since the fall of rotatory power after the addition of water was more rapid than in the case of samples of benzene which had been saturated by standing over water, the results here recorded can be explained most easily by supposing that the "dry" benzene already contained some substance which was potentially a catalyst, but which developed its catalytic activity only on the addition of water. This conclusion is in agreement with that already reached in paragraph (i) above, in comparing the behaviour of wet and dry benzene.

(iii) Subsequent experiments with wet benzene gave irregular values for the velocity coefficient, *e.g.*, 0·0003, 0·0008, 0·0005, and 0·0011, the first and fourth of these values being given by solutions of tetramethylglucose in benzene saturated with water, whilst the second and third were for mixtures of equal volumes of wet and dry benzene; but in no case was the velocity of mutarotation as low as that recorded for dry benzene in (ii) above.

The observations described under (i) to (iii) above can only be explained by applying to the sugars the view, already expressed in the case of nitrocamphor, that pure benzene has no appreciable catalytic properties of its own, but may acquire them by the addition of impurities. These impurities, however, must include other substances beside water, since the catalytic activity of wet benzene is not constant (like that of water or of the more aqueous mixtures of water and alcohol), but varies over a very wide range. Thus the lowest velocity recorded for a solution in wet benzene was only one-fortieth of the velocity in water; but in three other cases, in which equal care was taken to avoid contamination, velocities two, three, and four times as great as this minimum were observed; and in the one instance cited in paragraph (ii) above the velocity was of the same order as in water.

5. *Ethyl Acetate not a Complete Catalyst.*

(*a*) *Experiments with "dry" ethyl acetate.* The solvent was purified in the usual way with sodium carbonate and calcium chloride, and dried by distilling twice from phosphorus pentoxide. The readings in Table II (*a*) show that the rotatory power was steady within $\pm$ 0·02° during a period of about a day and that mutarotation then proceeded with increasing velocity, but always quite slowly, during a period of about a week, after which the main series of observations was stopped. At the end of this time, however, the rotatory power had only fallen by 0·2° on a total of about 3°. Moreover, the subsequent mutarotation was so slow

that, when a second sample of the solution was transferred after 48 days from the silica flask to a silica polarimeter tube, the action was found to be still incomplete. The transference of the second sample from the flask to the tube was, however, followed during the next 3 days by a more rapid mutarotation at the rate of about 0·1° per day. The early readings are shown graphically in Fig. 1, together with data for a solution in wet ethyl acetate.

TABLE II.

Mutarotation of Tetramethylglucose in Ethyl Acetate.

(4 g. in 100 c.c. examined in 2-dcm. silica polarimeter tubes at 20°.)

(a) *Dried.*		(b) *With 2·42% of water.*		
Time.	a_{5461}.	Time.	a_{5461}.	k (min.).
¼ hour	9·78°	⅓ hour	9·88°	—
1 ,,	9·80	1 ,,	9·88	—
2 hours	9·80	2½ hours	9·82	—
3½ ,,	9·79	4 ,,	9·82	0·00009
5 ,,	9·80	5 ,,	9·80	0·00009
7 ,,	9·81	6 ,,	9·80	0·00009
8 ,,	9·80	7 ,,	9·78	0·00009
10½ ,,	9·81	9½ ,,	9·71	0·00011
23 ,,	9·78	22 ,,	9·48	0·00011
32 ,,	9·75	31 ,,	9·31	0·00012
48½ ,,	9·74	47½ ,,	9·05	0·00012
55 ,,	9·71	54 ,,	8·97	0·00012
72 ,,	9·67	71 ,,	8·76	0·00012
79 ,,	9·64	78 ,,	8·65	0·00013
95 ,,	9·60	94 ,,	8·51	0·00012
152 ,,	9·58	151 ,,	8·16	0·00011
168 ,,	9·57	167 ,,	8·03	0·00011
*48 days	7·82	*48 days	†7·12	
49 ,,	7·72			k = 0·00011
50 ,,	7·64			
51 ,,	7·56	Half-change period = 95 hours (obs.).		

* Sample taken from a silica flask which had been kept in the thermostat at 20° during the whole of the preceding period.

† Slight rise in the next 2 days.

A "period of induction," such as that recorded above, is conclusive evidence of the existence of *a preliminary phase preceding and holding up the main action.* In the case of a mutarotation this phase may be either (i) the first of a series of successive chemical changes, differing from the subsequent stages only in that it does not produce any marked alteration of rotatory power (compare the mutarotation of camphorcarboxylamide and camphorcarboxypiperidide, J., 1913, **103**, 913), or (ii) a period of time during which a pure material is taking up the impurities that are needed to promote the change, or an impure material is getting rid of some foreign substance which inhibits it. These two alternatives can be distinguished by the regularity and constancy of the period of

induction in the first case, and by its irregularity in the second. Since Baker, Ingold, and Thorpe (*loc. cit.*) did not record any period of induction in the mutarotation of tetra-acetylglucose in ethyl acetate, and since we did not observe any period of induction in ethyl acetate to which water had been added, there can be no doubt that the period of induction now recorded was of the latter type. In particular, it appears probable that, when a period of induction was observed, we were fortunate enough to be working with a system from which some ingredient, essential for the promotion of the chemical change, was initially absent but gradually appeared in the solution during the course of the first 20 hours, whilst in the experiments in which no period of induction was recorded this essential catalyst was already present when the solution was first examined.

(*b*) *Experiments with "wet" ethyl acetate.* The acceleration, shown in Table II (*b*), which was produced by adding 2·4% of water to the "dry" ethyl acetate was very marked. If compared with the complete arrest of mutarotation during the first 10 hours in "dry" ethyl acetate, the ratio of the velocities is, of course, infinite; but even when the average velocity during the first week is taken as a standard of comparison, the change in the "wet" ethyl acetate was ten times as fast as in the dry solvent. If, however, we compare the acceleration produced by adding water to ethyl acetate with the normal velocity of mutarotation in water itself, we find that the activity of the water in ethyl acetate corresponds to an active mass which is less than half of its total concentration.

(*c*) *Comparison with previous observations.* If the data recorded above for the velocities of mutarotation in dry and wet ethyl acetate were plotted on a velocity–concentration diagram, they could only be joined by a diagonal line passing through the origin, of the same general character as the line * labelled "Theoretical for Lowry or Armstrong's Mechanism" in the diagram in which Baker, Ingold, and Thorpe (J., 1924, **125**, 281) plot their own experimental results as four points on a horizontal straight line labelled "Theoretical for Jacobson and Stelzner's

* This straight line is a graphical expression of the fallacy of identifying the activity of the water with its total concentration, rather than an expression of the essential requirements of a hydrate theory of catalysis. The responsibility for this line obviously belongs to the authors who drew it, and not to Lowry or Armstrong, whose names have been attached to it. In the same way, it would be unreasonable to hold Jacobson and Stelzner responsible for the horizontal line which expresses the fallacy that the velocity of isomeric change is independent of the concentration of the catalyst by which the change is determined.

Mechanism." It has already been suggested under (*a*) above that the failure of their line to pass through the origin was due to the use of incompletely purified materials; it is now necessary to inquire why our experiments show an increased velocity of mutarotation in presence of added water, whilst their data showed no such acceleration. The answer to this question is very simple, since it can be calculated that, even if the catalytic activity of the water were proportional to its total concentration, the acceleration produced by 1% of added water would increase the velocity coefficient at 20° by about 0·0001 only, *i.e.*, it would give rise to a velocity of the same order of magnitude as the lowest value recorded for mutarotation in dry benzene. The data in Table II show that in presence of a large excess of ethyl acetate the effect is even less than this, since 2·4% of water was required to give a velocity coefficient of the order of 0·0001. Since the half-change period for 2·4% of water is 95 hours, the "calculated" half-change periods for the concentrations of added water used by Baker, Ingold, and Thorpe would be 95 days for 0·1% of water and about a year for 0·025% of water. It has, moreover, been shown already that water in the presence of ethyl acetate is less efficient in promoting mutarotation than is water in the absence of ethyl acetate, obviously because the sugar has to compete with the solvent for possession of the catalyst. This effect is likely to be exaggerated when the concentration of the water is reduced, so that the excess of ethyl acetate is still larger; the effect of adding minute quantities of water would then be of a second order of minuteness, and could be detected only with the help of much more refined methods of examination than those which have been used hitherto.

6. *Experiments with Methyl and Ethyl Alcohols.*

(*a*) *Methyl alcohol.* Three new series of experiments on the velocity of mutarotation of glucose and of tetramethylglucose in dried methyl alcohol of known water content (purified by the method of Regnault as improved by Jones, McCombie, and Scarborough, J., 1923, **123**, 2694, and finally distilled from quicklime) are set out in Table III.

If we assume that the velocity of mutarotation would be increased about five-fold by the rise of temperature from 20° to 44·8°, the value recorded by Baker, Ingold, and Thorpe for glucose in "dry" methyl alcohol would (on reduction to the lower temperature and conversion to minutes as the unit of time) be about 0·0005 at 20° and would therefore be of the same order of magnitude as the values 0·0008, 0·0006, and 0·0004 which we have observed for glucose and for tetramethylglucose in methyl alcohol containing

TABLE III.

Mutarotation of Glucose and of Tetramethylglucose in Methyl Alcohol.

(In 6-dcm. glass polarimeter tubes at 20°.)

Glucose in dried methyl alcohol (99·8%) (shaken together and filtered).

Time.	a_{5461}.	$k \times 10^3$.
45 min.	6·32	—
1 hour	6·28	—
2 hours	6·19	0·71
3 ,,	6·06	0·83
4 ,,	5·92	[0·90]
5 ,,	5·85	0·82
6 ,,	5·74	0·84
9½ ,,	5·44	0·83
22 ,,	4·70	0·82
26½ ,,	4·52	0·83
30 ,,	4·42	0·82
46 ,,	4·09	0·83
49 ,,	4·06	0·81
70 ,,	3·96	0·70
74 ,,	3·92	[0·60]
78 ,,	3·90	0·75
96 ,,	3·82	
100 ,,	3·84	

$k = 0·00080$

Half-change period = 15 hours.

Glucose in dried methyl alcohol (99·5%) (shaken together and filtered).

Time.	a_{5461}.	$k \times 10^3$.
10 min.	8·24	—
25 ,,	8·21	0·63
1 hour	8·15	0·62
2 hours	8·04	0·62
3 ,,	7·95	0·59
4 ,,	7·86	0·59
6 ,,	7·68	0·59
22 ,,	6·62	0·59
31 ,,	6·25	0·59
47 ,,	5·81	0·59
56 ,,	5·64	0·56
Final	5·24	

$k = 0·00060$

Half-change period = 20 hours.

Tetramethylglucose in dried methyl alcohol (99·5%) (10 g./100 c.c.).

Time.	a_{5461}.	$k \times 10^3$.
1 hour	72·82	—
2 hours	72·52	0·39
4 ,,	71·92	0·40
6 ,,	71·34	0·40
9½ ,,	70·44	0·39
22½ ,,	67·65	0·39
30½ ,,	66·46	0·38
46½ ,,	64·36	0·38
55½ ,,	63·57	0·38
71 ,,	62·40	0·38
82½ ,,	61·24	0·45
95 ,,	61·23	0·39
102¾ ,,	60·93	0·39
10 days	59·76	

$k = 0·00039$

Half-change period = 30 hours.

rather more than 99½% MeOH. Our values for glucose at 20°, however, show an erratic behaviour that cannot be seen in the data for 44·8° (where only a single sample of alcohol and of sugar was examined), since the sample of methyl alcohol which had the larger water content had the smaller catalytic activity. Moreover, tetramethylglucose, which gives nearly the same velocity coefficients as glucose in water (and happens to give an identical velocity in aqueous methyl alcohol containing 20% of water), was now seen to change much more slowly than glucose, a result that must, we think, be attributed to the greater purity of the tetramethylglucose.

The fact that a finite velocity was observed for a solution in methyl alcohol of the same sample of tetramethylglucose which had exhibited an arrest of mutarotation in ethyl acetate and in chloroform is sufficient to prove that this residual velocity cannot have been due to impurities in the sugar. Moreover, since each 1% of added water has been found to increase the velocity of mutarotation by only about 0·00008 in minute-units at 20°, it is clear that a velocity of 0·0004 would correspond with the presence of about 5% of water in a sample which was shown by determinations of density to contain less than 0·5% of water. The

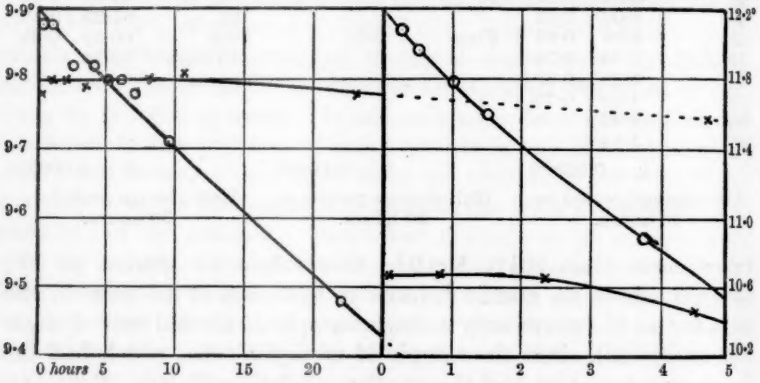
residual velocity of mutarotation of tetramethylglucose in methyl alcohol cannot therefore have been due either (i) to impurities in the sugar, or (ii) to water in the alcohol, and must therefore be attributed either (iii) to the presence in the alcohol of some unknown catalyst, other than water, or (iv) to catalysis by the alcohol itself, apart from the direct catalytic action of the small amount of water which it contained. The latter alternative is perhaps the more reasonable, but the former alternative cannot yet be excluded. If the alcohol is not a catalyst, it may be possible to establish this fact by using some more effective method of purification in order to produce an arrest of mutarotation in this solvent. If the alcohol

FIG. 1.

Mutarotation of tetramethylglucose in "dry" and "wet" ethyl acetate.
× *dry.* o *wet.*

FIG. 2.

Mutarotation of tetramethylglucose and glucose in "dry" pyridine.
o *glucose.* × *tetramethylglucose.*



is a catalyst, this direct proof will not be possible, but it is hoped that an indirect method of attack may lead to a definite solution of the problem.

7. *Experiments with Pyridine* (Fig. 2).

(*a*) *Glucose.* Data showing the mutarotation of glucose, and of tetramethylglucose in anhydrous pyridine at 20° are set out in Table IV. The velocity of mutarotation of glucose in a mixture of 1 part of pyridine with about 6 parts of water has been found to be perhaps 18 times more than in water. On the other hand, the velocity in "dry" pyridine as shown in Table IV (*a*) and (*b*) is about 15 times *less* than in water. This velocity may perhaps be reduced by further purification, but we have already proved that, when due allowance is made for differences of concentration, pyridine in the presence of an excess of water is at least 2000 times more efficient as a catalyst than pyridine in the absence of water.

TABLE IV.

Mutarotation of Glucose and Tetramethylglucose in Anhydrous Pyridine at 20°.

(a) *Glucose** (shaken and filtered).

Time (mins.).	α_{5461}.	$k \times 10^3$ (min.).
15	12·09°	—
30	11·97	[1·34]
60	11·79	1·14
90	11·60	1·12
125	11·44	1·03
225	10·88	1·06
390	10·14	1·03
1125	7·93	1·04
1585	7·17	1·07
Final (120 h.)	6·03	

$k = 0{\cdot}00107$

Half-change period = 9 hours.

(b) *Glucose* (shaken and filtered.) (Second sample of pyridine.)

Time (mins.).	α_{5461}.	$k \times 10^3$ (min.).
10	10·16°	—
20	9·99	—
30	10·02	1·0
45	9·94	1·1
60	9·87	1·0
90	9·73	1·1
135	9·60	0·9
195	9·35	1·0
225	9·18	0·9
385	8·83	0·8
Final	5·35	—

$k = 0{\cdot}0010$

Half-change period = 10 hours.

(c) *Tetramethylglucose* (1 g. in 25 c.c.; filtered).

Time (mins.).	α_{5461}.
5	10·67°
50	10·67
140	10·65
270	10·46
1280	8·43
1670	7·80

* The three readings of Behrend and Roth for the mutarotation of glucose in dried pyridine at 0° and with sodium light happen to fit almost perfectly on to this curve.

(*b*) *Tetramethylglucose.* In the case of tetramethylglucose, the rapid mutarotation shown in Table IV (*c*) was preceded by a " period of induction " (Fig. 2) during which mutarotation was arrested completely during a period of 2 hours. Mutarotation then began slowly, but proceeded with increasing speed, so that it was almost completed during the following night, but with the production of a green solution. The pyridine for this experiment had been dried with very great care, by a three-fold treatment with barium oxide, for use as a condensing agent in the preparation of co-ordination compounds; but it had not been purified in any other special way, and may have contained a mixture of bases, including the reactive α-derivatives of pyridine. Careful drying, therefore, stopped the action completely for a short time; but as soon as a sufficient supply of an auxiliary catalyst had been obtained the mutarotation was rapid, and proceeded to completion in a shorter period than in the corresponding experiment with glucose.

(*c*) Pyridine is a tertiary base of a particularly stable type, from which it would be impossible to remove a proton without the use of drastic chemical agents, such as are used in chlorination or nitration. We do not expect, therefore, to be able to repeat this observation with anhydrous ammonia which (like water) can either gain or lose a proton. The experiment might also be difficult

to repeat with a stronger base, since the velocity of mutarotation probably depends on the product (or some similar function) of the basic and acid dissociation constants of the medium, as well as of the sugar; a stronger base might therefore require only minute traces of water in order to develop a catalytic activity of sufficient intensity to produce an almost instantaneous mutarotation. This conclusion has an important bearing on the experiment with tetramethylglucose which has just been described, since the results observed would obviously follow if the liquid contained bases which *when acting in presence of water* had a higher catalytic activity than that which is developed by pyridine under the same conditions.

8. *Summary.*

(*a*) Although glucose is unsuitable for use in experiments on the arrest of mutarotation, the *tetramethylglucose* of Purdie and Irvine is an ideal sugar for this purpose, on account of its ready solubility in anhydrous solvents, and of the possibility of adequate purification by crystallising it from such solvents. Its behaviour has therefore been studied in chloroform, benzene, ethyl acetate, methyl alcohol and pyridine.

(*b*) The mutarotation in *chloroform* was (in one instance only) arrested during a period of 10 days, just as was formerly observed in the case of nitrocamphor; this arrest is attributed to the elimination of catalysts by carbonyl chloride derived from the chloroform by oxidation.

(*c*) The velocity of mutarotation in *benzene* was reduced from 0·0008 to 0·0001 by careful drying, but a very rapid mutarotation was produced by the addition of water; this was attributed to the possible presence in the benzene of water-soluble impurities which developed strong catalytic properties only after association with water.

(*d*) The mutarotation in *ethyl acetate* was preceded by a period of induction extending over about a day; this solvent, therefore, appears to possess no catalytic properties of its own in the absence of an auxiliary catalyst. In presence of small quantities of water, mutarotation proceeded without a period of induction.

(*e*) No arrest or period of induction was observed in the mutarotation of glucose in *methyl alcohol* or of tetramethylglucose in *methyl* or *ethyl alcohol*. It is therefore possible that methyl alcohol is a real catalyst for the mutarotation of the sugars, although thirty times less efficient than water; but this view is based only on negative evidence, since it is possible that further purification may reduce (or even eliminate) the small residue of catalytic activity which it appears to possess.

(*f*) The velocity of mutarotation of glucose in *pyridine*, to which no water has been added, is very small, but no arrest of mutarotation has yet been recorded. The mutarotation of tetramethylglucose in pyridine, however, was preceded by a short period of induction; this shows that the change is not spontaneous, but depends on the presence of an auxiliary catalyst.

(*g*) A clear distinction is drawn between (i) *inactive solvents* such as chloroform, which have no catalytic properties; (ii) *ampholytic solvents* such as water, which can act as *complete catalysts*; (iii) solvents such as pyridine, which are not catalysts when pure, but develop catalytic properties in presence of an *auxiliary catalyst*; the *mixed catalysts* formed in this way are more efficient than the *complete catalysts*, and often give rise to a mutarotation which is too fast to be followed experimentally.

We desire to express our thanks to the Department of Scientific and Industrial Research for a maintenance grant to one of us (E. M. R.) during the period in which this research was carried out.

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[*Received, March 4th*, 1925.]

CXC.—*The Constitution of Soap Solutions in Presence of Electrolytes. Potassium Laurate and Potassium Chloride.*

By WILLIAM CLIFFORD QUICK.

By combining measurements of conductivity with those of osmotic activity (*e.g.*, freezing-point depression), the nature and amount of the various constituents of soap solutions have been deduced.* The addition of a salt necessitates the use of a third method. The determination of the transference of each of the constituents of the solution during electrolysis is perhaps the most decisive physicochemical method, when it is applicable, for it decides beyond question what are the constituents which conduct the current. In the present study, potassium laurate was chosen as a typical and stable soap, soluble at the ordinary temperature even in the presence of large amounts of potassium chloride. All three methods have been made use of and it has been shown that soap and salt mutually

* For references, see "The Study of Soap Solutions and its Bearing upon Colloid Chemistry." Union Internationale de la Chimie Pure et Appliquée, Cambridge, June, 1923; *J. Soc. Chem. Ind.*, 1923, **42**, 615; *Chim. et Ind.*, 1924, **11**, 3; *Amer. Dyestuff Rep.*, 1923, **12**, 822.

depress each other's dissociation; further, a value is deduced for the hydration of the colloid in solution which agrees with that previously determined by the method of ultrafiltration.

EXPERIMENTAL.

Materials.—The purest materials obtainable were used in all these experiments. In migration experiments 1 to 5 the potassium laurate used (from Kahlbaum) was 0·5% (equiv.) alkaline. The potassium sulphate and chloride employed were Kahlbaum's "zur Analyse." The 7% solutions of the latter are barely alkaline to phenolphthalein; which would very slightly affect the anode and cathode results in opposite directions. The potassium chloride was heated in a silica dish before the solutions were made up. In migration experiments 6 and 9 the potassium laurate was made from Kahlbaum's lauric acid (*M* 199·18) and pure potassium hydroxide (see Bunbury and Martin, J., 1914, **105**, 417). All the precautions described in previous communications were taken with standard solutions, solvents, vaselin, and apparatus.

Conductivity.—A complete series of conductivity measurements at 18° has been carried out with a solution containing 1 g.-mol. of potassium laurate in 1 kg. of water ($1{\cdot}0N_w$) to which potassium chloride was added in quantities varying from 0·5 mol. to 3·5 mols. ($3{\cdot}5N_w$). The cell was of the special high-resistance type described by McBain, Laing, and Titley (J., 1919, **115**, 1282).

Osmotic Activity.—The osmotic activity of the same series of mixtures as those used in the conductivity measurements has been determined by the method of dew-point lowering (McBain and Salmon, *J. Amer. Chem. Soc.*, 1920, **42**, 426). The lowering of freezing-point method is not applicable in the case of these mixtures, although it can be used with pure potassium laurate solutions up to $1{\cdot}0\ N_w$, because addition of electrolyte greatly reduces the solubility of curd fibres (compare J., 1922, **121**, 1320).

Electrolytic Migration.—The migration apparatus was the same as that used by McBain and Bowden (J., 1923, **123**, 2417). Guard solutions of potassium sulphate (7%) were most satisfactory for solutions containing potassium laurate and potassium chloride (up to $1{\cdot}0N_w$ with respect to each), being of the correct density to give a sharp boundary between guard solution and soap solution, but not of sufficient concentration to cause salting out. For the mixture $1{\cdot}0N_w$-potassium laurate and $2{\cdot}5N_w$-potassium chloride, even saturated solutions of potassium sulphate failed to give a clear boundary line. A solution containing 7% of potassium sulphate and 12% of sucrose was finally used. Sucrose, as Washburn has shown (*J. Amer. Chem. Soc.*, 1909, **31**, 322), has no tendency to

move with the current, and although any slight oxidation at the anode would have a corresponding effect on the potassium value, the experiment would be otherwise unaffected by its presence. All solutions were clear and homogeneous when measured, except for a slight cloudiness at the anode to be mentioned later.

To introduce the most viscous solution, namely, $2{\cdot}5N_w$-potassium chloride and $1{\cdot}0N_w$-potassium laurate, into the apparatus, a pipette closed at the bottom and having a fairly large hole in each side was used, in order to ensure a sharp boundary with the guard solution. Wide-mouthed pipettes were used for the removal of the solution from the apparatus. Even with these precautions the handling of the viscous liquid was so slow that the analytical data were considerably affected. The results, which are not given in the tables, show from analyses at the anode that the soap carries at the least 3—4% and at the most 10% of the total current. Analysis at the cathode gave a migration number of 0·48 for the chlorine, thus leaving a migration number of 0·02 or about 4% of the current for the soap. The soap solutions containing less salt were quite mobile.

The total current was measured by a silver coulometer on each side of the apparatus, any electrical leak thus being detectable. The best deposits of silver were obtained by using 10% solutions of silver nitrate with currents of 17 to 20 milliamps. Smaller currents tend to give loose deposits which are difficult to wash without loss of silver. With good deposits of silver, the coulometers agreed to 0·1%. By passing the current for about 2 hours, a deposit of about 0·16 g. of silver was obtained.

Analytical Methods.—After the passage of the current seven portions of the solution were analysed. In experiments 1 to 5 McBain and Bowden's method of soap analysis (*loc. cit.*) was used. The results thus obtained, however, were inaccurate, and in all later experiments the following method was used. A known quantity (excess) of $0{\cdot}5N_v$-sulphuric acid was added to a weighed portion of the solution, the mixture was shaken with three successive quantities of about 25 c.c. of chloroform, the chloroform solution of lauric acid removed, and the excess of sulphuric acid in the aqueous layer titrated with $0{\cdot}1N_v$-sodium hydroxide. The solution of lauric acid was boiled to expel carbon dioxide and, while still hot, titrated with $0{\cdot}25N_v$-alcoholic sodium hydroxide and phenolphthalein; by the careful addition of water as the titration proceeded a good end-point was obtained in a clear homogeneous solution.

The chloride in the aqueous layer was then estimated gravimetrically as silver chloride. In the anode and cathode portions containing the potassium sulphate from the guard solutions special

care was taken to avoid the precipitation of silver sulphate. The solution was diluted to about 600 c.c. before precipitation, and a larger quantity than usual of nitric acid was added, and silver nitrate only in slight excess. A small sample of the "middle-middle" portion (MM) was reserved for qualitative testing for sulphate in each experiment. At least one sample of the original mixture was analysed in each migration experiment.

Calculation of Data.—All analytical data are expressed in weight normality (N_w). The weights of potassium laurate and potassium chloride were obtained from the analysis, and that of the water by difference. The equivalent change of each constituent produced by electrolysis was referred to the weight of the same constituent associated with an equal weight of water in the original mixture. In calculating the change in the concentration of potassium ion the total potassium must be considered, being the equivalent of the $N/2$-sulphuric acid used to split up the soap + potassium associated with chloride (= total equivalent of chloride by analysis).

The weights of oxygen and hydrogen evolved at the anode and the cathode, as calculated from the coulometer reading, are added to the weights. Each experiment gives four independent determinations of the migration number of potassium, but only two of laurate and chloride.

The total number of equivalents transported should be equal to the coulometer equivalents; *i.e.*, if the sign of the migration number of the anion or the kation is changed, then the migration of anion + kation should be equal to ± 1. For example, the algebraic sum of the quantities of potassium, laurate and chloride transported should equal unity. This fact provides a check on the accuracy of the data in each experiment where the data are complete.

Experimental Data.—The conductivity measurements are given in Table I. The values given as "molecular conductivity" (μ) are calculated with respect to normality of total potassium element.

Table II contains the results obtained from determinations of the lowering of dew point.

Table III gives the results of migration experiments using solutions of potassium laurate without added salt. The data for $1{\cdot}0N_w$-solution confirm Bowden's result obtained at this concentration, and comparison of migration 6 with his data clearly shows the greater accuracy of the new method of analysis.

Table IV contains migration data for mixtures of $1{\cdot}0N_w$-potassium laurate and $1{\cdot}0N_w$-potassium chloride. The migration of chlorine takes a peculiar form, a large gain in the anode compartment being followed by a fairly large loss in the adjoining anode middle

TABLE I.

Conductivities at 18°.

Solutions $1{\cdot}0N_w$ with respect to potassium laurate.

KCl (N_w).	Spec. cond. $\kappa \times 10^{-2}$.	True density at 18°.	Mol. cond. μ.	KCl (N_w).	Spec. cond. $\kappa \times 10^{-2}$.	True density at 18°.	Mol. cond. μ
—	3·824			1·5	13·31	1·0665	67·41
	3·889		47·09		12·50		63·29
	3·886			2·0	15·40	1·0819	65·76
0·5	7·226	1·0346	59·35		15·38		65·68
	7·174		58·93	2·5	17·87	1·0972	66·27
0·7	8·289	1·0423	59·71	3·0	20·07	1·1126	65·90
1·0	10·064	1·0525	62·72		19·88		65·30
	10·090		62·87	3·5	21·97	1·1275	64·96

The value for $1{\cdot}0N_w$-potassium laurate without salt, given for comparison, is from McBain, Laing, and Titley (J., 1919, **115**, 1282).

Cell constant at the beginning of the series, 14·02; at the end, 14·05.

TABLE II.

Dew-point Lowering and Osmotic Activity at 18°.

Solutions $1{\cdot}0N_w$ with respect to potassium laurate.

KCl (N_w).	Dew-point lowering.	Mean.	KCl (N_w).	Dew-point lowering.	Mean.
0·5	0·45, 0·41, 0·44, 0·45	0·44	2·0	1·27, 1·30	1·28
0·7	0·57, 0·57	0·57	2·5	1·41, 1·43, 1·41	1·42
1·0	0·77, 0·78, 0·75, 0·77	0·77	3·0	1·69, 1·73	1·70
1·5	1·02, 0·96, 1·04	1·01	3·5	(1·88), 2·07, 1·97	1·9(7)

Apparent concentration of crystalloid = dew-point lowering/0·30.

TABLE III.

Migration Data for $1{\cdot}0N_w$-*Potassium Laurate* (without added salt).

Expt. 2. Temp. 18°. Analysis of original solution: $K = 0{\cdot}970N_w$, $L = 0{\cdot}963N_w$. Current of 22 milliamps. passed for 105 mins. Coulometer equiv. = 0·001241 equiv. of silver.

Portion.	Equivalents change. K.	L.	Transference number (n). K analysis.	L analysis.	Mean.
Anode	−0·459	+0·634			
AM	+0·030	+0·094	0·55	0·81	
AMM	−0·018	+0·083			
MM	+0·059	+0·168			$n = 0{\cdot}53$
CMM	−0·041	+0·048			
CM	+0·028	+0·049	0·46	0·31	
Cathode	+0·557	−0·402			

Expt. 3. Temp. 14·5°. Analysis of original solution: $K = 1{\cdot}002N_w$, $L = 1{\cdot}001N_w$. Current of 20 milliamps. passed for 135 mins. Coulometer equiv. = 0·001697 equiv. of silver.

Anode	−0·434	+0·540			
AM	−0·037	−0·016	0·54	0·54	
AMM	+0·006	+0·014			
MM	−0·008	−0·007			$n = 0{\cdot}51$
CMM	−0·005	−0·007			
CM	±0·000	±0·000	0·47	0·50	
Cathode	+0·533	−0·494			

Table IV.

Migration Data for 1·0N$_w$-Potassium Laurate + 1·0N$_w$-Potassium Chloride.

Expt. 6. Temp. 14°. Analysis of original mixture : Soap, K = 0·984N_w, L = 0·969N_w; KCl = 0·995N_w; total K = 1·979N_w. Current of 21 milliamps. passed for 120 mins. Coulometer equiv. = 0·01591 equiv. of silver.

	Equivalents change.			Transference numbers.			
Portion.	K.	L.	Cl.	K.	L.	Cl.	Mean values.
Anode	*	+0·283	—				
AM	−0·61	−0·094	—	(0·61)	0·21	—	L = 0·23
AMM		+0·025	—				
MM	−0·03	−0·010	±0·00				Cl = 0·31
CMM	−0·01	−0·023	+0·007				(L + Cl) as
CM	−0·06	−0·023	−0·005	0·41	0·26	0·31	K = 0·46
Cathode	+0·46	−0·217	−0·314				K = 0·49

* This value for K is obtained if Cl = 0·30.

Expt. 4. Temp. 15·5°. Analysis of original mixture : Soap, K = 0·991N_w, L = 0·974N_w; KCl = 0·997N_w; total K = 1·988N_w. Current of 19·5 milliamps. passed for 130 mins. Coulometer equiv. = 0·001543 equiv. of silver.

Anode	−0·44	+0·494	+1·058				
AM	—	−0·299	—	—	+0·14	—	L = 0·17
AMM	+0·016	−0·049	−0·132				
MM	−0·04	−0·021	−0·026				Cl = 0·26
CMM	±0·00	+0·006	−0·032				(L + Cl) as
CM	−0·134	−0·072	−0·161	(0·70)	0·20	0·26	K = 0·54
Cathode	+0·836	−0·132	−0·036				

Expt. 5. Temp. 15°. Analysis of original mixture : Soap, K = 0·991N_w, L = 0·974N_w; KCl = 0·997N_w; total K = 1·988N_w. Current of 20 milliamps. passed for 165 mins. Coulometer equiv. = 0·00194 equiv. of silver.

Anode	+0·646	+0·522	+1·072				
AM	−0·736	−0·210	−0·516	(0·26)	0·25	0·43	(L + Cl) as
AMM	−0·124	−0·046	−0·089				K = 0·52
MM	−0·040	−0·018	−0·030				L = 0·18
CMM	−0·014	±0·000	−0·012				
CM	−0·143	−0·004	−0·161	(0·77)	0·12	(0·16)	Cl = 0·33
Cathode	+0·913	−0·118	±0·000				

Expt. 7. Temp. 13°. Analysis of original mixture : Soap, K = 1·001N_w, L = 0·997N_w; KCl = 1·005N_w; total K = 2·006N_w. Current of 21 milliamps. passed for 120 mins. Coulometer equiv. = 0·001567 equiv. of silver.

Anode	+0·470	+0·516	+0·950				
AM	−0·742	−0·218	−0·517	−0·48	+0·24	+0·31	(L + Cl) as
AMM	−0·207	−0·055	−0·126				K = 0·51
MM	−0·054	−0·003	−0·051				
CMM	−0·051	+0·002	−0·032				K = 0·50
CM	−0·193	−0·012	−0·157	+0·51	−0·14	−0·29	L = 0·19
Cathode	+0·756	−0·129	−0·097				Cl = 0·30

Final values for migration numbers in 1·0N_w-K Laurate + 1·0N_w-KCl ..... { K = 0·47, L = 0·19, Cl = 0·32 }

i.e., K + L + Cl = 0·98.

(AM) portion; whilst at the cathode there is scarcely any loss. A similar effect is seen in the apparent movement of the fatty acid and potassium. This phenomenon cannot be due to mixing,

as the boundaries remain undisturbed throughout; it may be explained, however, when we remember that the soap mixture is more than twice as concentrated as the guard solution and therefore tends to imbibe water.

Discussion.

McBain and his collaborators have shown that under given conditions the constituents of a soap solution, *viz.*, neutral colloid, ionic micelle, and simple crystalloid, are in true, reversible equilibrium. The work of McBain and Burnett (J., 1922, **121**, 1320) has also established the fact that the equilibrium colloid $\rightleftharpoons$ crystalloid in any particular solution under given conditions is remarkably definite in presence of added electrolyte. It may therefore be expected that any or all of the above-mentioned constituents of a pure soap solution will be affected in a definite and reproducible manner by the addition of a salt. We must consider the possibility of change not only in the proportions of micelle and neutral colloid but also in their nature.

Trustworthy information on the subject of transport numbers is essential for any solution of the problem. The fraction of the total conductivity of the solution due to any one constituent is dependent on its concentration and mobility and equally on the total conductivity of the solution. Therefore the total conductivity must be resolved as the sum of the conductivities of all the various conducting constituents according to an expression (Laing, *J. Physical Chem.*, 1924, **28**, 673) of the form

$$n = (cv + c_1m_1f_1 + c_2m_2f_2)/\mu,$$

where m = number of chemical equivalents of a particular constituent which carry one electric charge, f = conductivity in mhos of one chemical equivalent of the same constituent (v for Cl′, f_1 for ionic micelle, f_2 for neutral colloid), n = migration number, μ = conductivity in mhos of that amount of solution containing 1000 g. of water and c equivalents of the constituent, and c = number of chemical equivalents of the constituent per 1000 g. of water.

The value obtained for the transport of total potassium in these mixtures, 0·47, allows us to conclude that there can be very little movement of neutral colloid. If m_2f_2, the effective mobility of the neutral colloid, had been as great in pure soap solution, *viz.*, 20 mhos, its apparent migration towards the anode, $n_2 = c_2m_2f_2/\mu$, would have been 0·10 in 1·0N_w-potassium laurate + 1·0N_w-potassium chloride. But the total movement of potassium, 0·47, towards the cathode differs by 0·03 unit from the value, 0·50, that would be given either by potassium chloride or by potassium ion + ionic micelle alone. Hence the effective mobility of the neutral colloid

is $20 \times 0{\cdot}03/0{\cdot}10 = 6$ mhos. Mukherjee and Roy (J., 1924, **125**, 476) have pointed out that the effect of the addition of an electrolyte with univalent ions to a charged colloid is gradually to neutralise the charge by electrical adsorption of ions of opposite sign to that of the charged colloid, reversal of sign being impossible. Thus we might expect the "neutral colloid," which is only very slightly charged in pure soap solutions, to move still less in these mixtures.*

A second main conclusion to be drawn with certainty from the migration data for $1{\cdot}0N_w$-potassium laurate + $1{\cdot}0N_w$-potassium chloride is that the soap conducts nearly two-fifths of the current. This corresponds to the conducting power of the soap in $1{\cdot}0N_w$-potassium laurate alone. If we assume that the mobility of the ionic micelle in the mixture is approximately the same as in $1{\cdot}0N_w$-potassium laurate alone, the mobilities of $K^{\cdot}$, Cl' and $(L')_n$ are identical. From Table V the concentration of $K^{\cdot}$ is 0·97 and that of $(L')_n + Cl'$ is necessarily equivalent to it, making a total concentration of conducting constituents of $1{\cdot}94N_w$. Hence the concentration of $(L')_n = 1{\cdot}94 \times 0{\cdot}19 = 0{\cdot}37N_w$, and the concentration of $Cl' = 1{\cdot}94 \times 0{\cdot}31 = 0{\cdot}60N_w$. Thus, unless we are to assume that the mobility of the ionic micelle is very greatly enhanced, its concentration cannot be greatly decreased by this concentration of added electrolyte. We should, however, expect some increase in the mobility of the micelle, which leads to the conclusion that its concentration must be less than in $1{\cdot}0N_w$-potassium laurate alone and that the concentration of the chlorine ion is rather higher than $0{\cdot}60N_w$. In the absence of soap the concentration of chlorine ion in $1{\cdot}0N_w$-potassium chloride as indicated by osmotic methods is $0{\cdot}74N_w$.

In the case of the mixture $1{\cdot}0N_w$-potassium laurate and $2{\cdot}5N_w$-potassium chloride the soap still conducts a fraction of the current, but so small as to indicate that dissociation into ionic micelle has been diminished by the higher concentration of chloride. The experimental error in migration 9 allows us to place the migration of soap in $1{\cdot}0N_w$-potassium laurate + $2{\cdot}5N_w$-potassium chloride not higher than a maximum of 10%, which gives the concentration of ionic micelle as $0{\cdot}18N_w$, assuming its mobility the same as $K^{\cdot}$ and Cl'. As will be seen later, however, we have in the present case evidence that the hydration of the soap is decreased by the added electrolyte (compare McBain and Taylor, J., 1919, **115**, 1300; 1921, **119**, 1369; Bennett, J., 1924, **125**, 1971, etc., where added electrolyte causes dehydration of curd fibres of palmitate). In this case we should expect a micelle of greater mobility and thus

* A further detailed study will be published by Dr. M. E. Laing.

we may conclude that one effect of the added salt is the repression of the dissociation of the colloidal electrolyte.

The Hydration of the Soap.—The data also afford definite indications of the degree of hydration of the soap in solution. In previous communications from this laboratory it has been shown that the anion of the soap is an aggregate of fatty acid ions retaining their full electric charge and carrying water of hydration. In all except very dilute solutions the remainder of the soap is almost entirely in the form of neutral colloid. We may write: Neutral colloid = $(\text{K Laurate})_x,yH_2O$ and ionic micelle = $(L')_n,mH_2O$. In pure soap solutions also the ionic micelle has a mobility at least equal to that of the potassium ion or chlorine ion (64). Evidently the mobility will be influenced by changes in the degree of hydration. If we assume that the mobility of the ionic micelle is the same as in pure soap solutions, the mobilities of the potassium ion, the chlorine ion, and $(L')_n$ are each 65 mhos, which gives $u + v = \mu_\infty = 130$. The concentration of $K^\cdot$ is μ_v/μ times N_w of the total potassium in the solution. The total crystalloid in these mixtures is total potassium ion plus chlorine ion plus undissociated potassium chloride, *i.e.*, the concentration of the total crystalloid is (Normality of total chlorine plus potassium ion) or total chloride plus $\mu_v/\mu_\infty \times N_w$ of the total potassium in the solution. Now the osmotic activity gives the apparent concentration of crystalloid, but this value is enhanced because a portion of the solvent water is removed by hydration of the soap. Therefore we can calculate the hydration by means of the difference between *the concentration of total crystalloid* deduced from conductivity data and *the apparent concentration of crystalloid* obtained from the dew-point lowering. Take, for instance, the data for the solution $1{\cdot}0N_w$-potassium laurate and $1{\cdot}0N_w$-potassium chloride: $\mu_v/\mu_\infty = 62{\cdot}79/130$. Therefore $[K^\cdot] = 0{\cdot}97N_w$ and [total crystalloid] $= 1{\cdot}97N_w$. The concentration of total crystalloid deduced from the lowering of dew-point is $2{\cdot}57N_w$. Therefore hydration = 23% of the total water (55 mols.) = 12·8 mols. of water per equivalent of soap.

Now, these values are not greatly affected by any possible deviations of the mobility of the ionic micelle from its assumed value, on account of decreased hydration. From the migration data we see that only 18% of the value of μ_∞ is due to the ionic micelle. Thus even an increase in the mobility of the micelle of one-fifth would only make $\mu_\infty = 135$; whence the mobility of $K^\cdot = 0{\cdot}93$ and the hydration = 13·7, instead of 0·97 and 12·8, respectively.

In higher concentrations of potassium chloride the values of the concentration of $K^\cdot$ and of the hydration of the soap are even less

dependent on the mobility of the ionic micelle, as a still smaller fraction of the total conductivity is due to the ionic micelle. In Table V, therefore, are given the values of the concentration of K$^{\cdot}$ and of the hydration corresponding to a mobility of ionic micelle = 65 (= K$^{\cdot}$ = Cl′). We may regard these values as being correct to within 1 mol. of H_2O and $\pm$ 0·02N_w-K$^{\cdot}$. This value, 12·8 mols. per equivalent, for the hydration of the soap in the solution 1·0N_w-potassium laurate + 1·0N_w-potassium chloride is in good agreement with the value, > 11·8, obtained by McBain and Jenkins (J., 1922, **121**, 2325) by the method of ultrafiltration. The experimental error in the case of the solution 0·5N_w-potassium chloride + 1·0N_w-potassium laurate is larger than that for a solution of higher concentration, a difference of $\pm$ 0·01° in the dew-point lowering corresponding with a difference of $\pm$ 1·1 mols. of water in the hydration value.

TABLE V.

Concentration (N_w) of the Constituents and the Total Hydration of the Soap in Solutions of 1·0N_w-Potassium Laurate containing added Potassium Chloride at 18°.

KCl.	K$^{\cdot}$.	Total crystalloid.	Hydration. Mols. H_2O : 1 mol. KL.	KCl.	K$^{\cdot}$.	Total crystalloid.	Hydration. Mols. H_2O : 1 mol. KL.
0·5	0·68	1·18	11 ($\pm$1·1)	2·0	1·52	3·52	9·6
0·7	0·78	1·48	12·2	2·5	1·78	4·28	5·2
1·0	0·97	1·97	12·8	3·0	2·02	5·02	6·3
1·5	1·26	2·76	10	3·5	2·25	5·75	6·9

No stress can be laid on the apparent minimum in the presence of 2·5N_w-potassium chloride, although at this same concentration the conductivity and possibly also the viscosity has a maximum value.

The values in Table V for the concentrations of the potassium ion in the solutions 1·0N_w-potassium laurate + 0·5N_w-potassium chloride and 1·0N_w-potassium laurate + 1·0N_w-potassium chloride do not agree with the respective values of 0·38N_w and 0·79N_w obtained by Salmon from *E.M.F.* measurements (J., 1922, **121**, 711). Also his value of 0·09N_w for the ionic micelle in the solution 1·0N_w-potassium laurate + 1·0N_w-potassium chloride appears to be much too low in view of the migration values obtained for this solution. Presumably the correction assumed by Salmon for diffusion potential is inadequate.

The value of Cl′ = 0·60N_w obtained from the transport of chloride in 1·0N_w-potassium laurate + 1·0N_w-potassium chloride and the molecular conductivity of the same solution indicates that the soap likewise diminishes the dissociation of the potassium chloride.

Summary.

Accurate determinations have been made of the transport of each of the constituents of a solution containing potassium laurate and potassium chloride during electrolysis.

In a solution which is weight normal with regard to both salt and soap, the quantities of potassium, laurate and chloride ions transported are 0·47, 0·19, and 0·32 equivalent, respectively.

Apparently, therefore, the undissociated soap (neutral colloid) scarcely moves in this solution, and the ionic micelle does not contain appreciable quantities of undissociated soap. This confirms previous work showing that the ionic micelle is a hydrated colloidal aggregate of simple fatty ions.

Since the migration of the potassium ion, 0·47, is nearly the same as in solutions of pure potassium chloride, whereas the migration number of the chlorine ion is only 0·32, only three-fifths of the total current is carried by potassium chloride, the remaining two-fifths being carried by ionised soap (ionic micelle).*

Salt and soap therefore mutually diminish each other's dissociation. Even when 2·5 equivalents of salt are added to a weight normal solution of laurate, there is still an appreciable quantity of dissociated soap (ionic micelle).

These data in conjunction with measurements of conductivity and of dew-point lowering enable us to evaluate the constituents present in these mixed solutions. Further, they show that the hydration of potassium laurate in 1·0N_w-solution, where it is entirely colloidal (neutral colloid and ionic micelle), amounts to 12·8 mols. of water per equivalent of laurate. This confirms the value found by McBain and Jenkins by the wholly independent method of ultrafiltration.

An improvement in the method of analysis of solutions of soap is described in which filtration is replaced by extraction.

My thanks are due to Professor J. W. McBain, F.R.S., at whose suggestion the work was carried out, for his constant interest and advice.

University of Bristol. [*Received, March 31st,* 1925.]

* The mobilities of chlorine ion and ionic micelle are comparable with each other.

CXCI.—*Plant Cuticles. Part I. Modern Plant Cuticles. Studies in the Composition of Coal.*

By Vernon Howes Legg and Richard Vernon Wheeler.

A series of researches on plant cuticles has been undertaken with a view ultimately to determine the constitution of cuticle as it occurs in bituminous coals, in conformity with the scheme of research outlined by Stopes and Wheeler (Monograph on the Constitution of Coal, London, 1918, p. 26).

The term cuticle was first used by Brongniart (*Ann. Sci. Nat.*, 1830, **21**, 427) to denote the outer protective covering which is common to all parts of plants. Although from a botanical point of view the cuticle is a well-defined and easily recognisable constituent of the plant, yet its chemical nature has remained obscure. The only chemical research on modern plant cuticle recorded in the literature appears to have been carried out by Frémy (*Compt. rend.*, 1859, **48**, 667; 1881, **92**, 926; 1885, **100**, 19) on the cuticle from ivy, apple and agave. By means of boiling alkalis, Frémy resolved the cuticle from agave, after extraction with solvents, into two acids which were isolated in the form of their corresponding salts: a solid acid which he termed stearocutic acid (C, 75·0; H, 10·7; O, 14·3%), characterised by the insolubility of its potassium salt in water; and a semi-liquid acid, oleocutic acid (C, 66·7; H, 7·9; O, 25·4%). Frémy concluded that the characteristic constituent of cuticle, termed by him cutin or cutose, consists of a mixture of these two acids in the proportion of one part of stearocutic to five parts of oleocutic acid. He observed (*Ann. Sci. Nat.*, 1882, **8**, 360) that similar products were obtained from purified cork, from which he concluded that suberin, the characteristic constituent of cork, is an impure form of cutose. No evidence was adduced in support of this suggestion. Similar views have been advanced by Mitscherlich (*Annalen*, 1850, **75**, 305), von Höhnel (*Bot. Z.*, 1878, **3**, 81) and by van Wisselingh (*Arch. Néerland.*, 1886, **20**, 95; 1888, **22**, 253; 1892, **26**, 305; 1895, **29**, 373), chiefly as a result of microchemical observations. Since it will be shown in the present paper that the compounds which can be isolated from modern plant cuticle are indeed closely related both in properties and in composition to those obtained from cork, a brief reference should be made to the chemistry of the latter material.

By the action of alcoholic potash on purified cork, Kügler (Ueber das Suberin, Strassburg, 1884; *Arch. Pharm.*, 1884, **22**, 217) isolated stearic acid together with a crystalline acid known as

phellonic acid ($C_{22}H_{42}O_3$: C, 74·6; H, 11·7%), which, like stearocutic acid, forms a potassium salt insoluble in water. On the other hand, Gilson (*La Cellule*, 1890, **6**, 63), using the same reagent, isolated phellonic acid; a semi-liquid acid called suberinic acid, $C_{17}H_{30}O_3$; and a solid acid, phloïonic acid, for which he suggested the formula $C_{11}H_{21}O_4$ (an impossible one, assuming normal valencies). Schmidt (*Monatsh.*, 1904, **25**, 227, 302; 1910, **31**, 347) confined his attention more particularly to phellonic acid and in his first paper suggested the probable structure of this acid.

Some confusion has arisen from the use of the terms adipocellulose and cutocellulose by Cross and Bevan ("Cellulose," London, 1916, p. 225) and Cross and Dorée ("Researches on Cellulose, 1910—1921"; London, 1922, p. 188) for cork and cuticle respectively. In the latter, at all events, the outer layer of cuticle (as distinct from the cutinised layer) does not contain cellulose and the term cutocellulose is a misnomer. This point has been dealt with by Priestley (*The New Phytologist*, 1921, **20**, 17).

For the purpose of the present research, the cuticle from the *Agave americana* was chosen (as representing a typical modern plant cuticle) because the agave, in common with other tropical and sub-tropical plants, has a comparatively thick cuticle. The *Agave americana*, the most familiar species of agave, is a native of tropical America and is more familiarly known in this country as the century plant or American aloe. The plant consists of a large rosette of thick fleshy leaves around a central stem. It flowers only once in a number of years.

The crude cuticle, apart from about 4% of inorganic material, consisted only of carbon, hydrogen, and oxygen. A series of analyses on the material from different sources showed variations in composition between C 58·5 to 64·5 and H 8·8 to 9·3%, according to the age of the leaves, the cuticle from the most mature leaves containing most carbon and hydrogen.

By extraction with solvents it was found possible to resolve the crude material into four distinct classes of compounds, differing widely in properties and compositions: (1) Water-soluble material, 10%, containing about 48% of carbon; (2) wax, 15%, soluble in alcohol, benzene, and chloroform, containing about 79% of carbon; (3) cellulose, 14%, soluble in cuprammonia solution; and (4) a residue, 60%, insoluble in all the foregoing solvents and giving on analysis a consistent value for carbon of about 68%. This purified residue may be regarded as the characteristic constituent of cuticle and can be conveniently referred to by the term *cutin*. Our study has been chiefly of this residue. Three methods of attack have been employed: (1) Treatment with alcoholic potash; (2) destructive

distillation for the examination of liquid and gaseous products; and (3) oxidation.

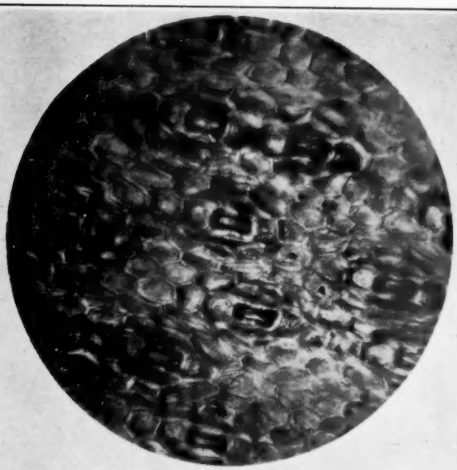
After a comparatively short treatment with alcoholic potash, more than 90% of the cutin was resolved. Preliminary experiments showed that the alcoholic solution consisted almost entirely of a mixture of the potassium salts of different acids. Neither glycerol nor any other alcohol could be detected. A separation of the acid products was first effected by the somewhat complicated process employed by Gilson (*loc. cit.*), but a shorter method was subsequently worked out, based on the varying solubilities of the potassium salts in water, whereby almost identical products were isolated.

The chief product resulting from the action of alcoholic potash on cutin consists of a mixture of two semi-liquid acids which form potassium salts soluble in cold water. The greater portion of this mixture consists of an acid which forms a copper salt soluble in alcohol, whereas the copper salt of the remaining acid is insoluble in alcohol, so that a separation of the mixture into its constituent acids could be effected in this manner. Both acids (which are similar in composition) have a lower carbon content than the suberinic acid isolated by Gilson from cork, but in other respects their properties agree with those described for that acid. The analytical data, given in the experimental part of this paper, are in agreement with the formula $C_{26}H_{50}O_6$ for the acid obtained from the copper salt soluble in alcohol, and with the formula $C_{13}H_{22}O_3$ for the acid from the copper salt insoluble in alcohol. So far as we know, the occurrence of these acids in nature has not hitherto been recorded. We suggest that the names *cutic acid* for the former, which occurs in the greater quantity, and *cutinic acid* for the latter, would be appropriate.

In addition, two other acids have been isolated from the cutin, though in much smaller quantities, in the form of their sparingly soluble and insoluble potassium salts. From the sparingly soluble potassium salt the corresponding acid was obtained as a white, crystalline material which appears to be identical in composition and properties with the phloïonic acid isolated by Gilson from cork, but for which the formula $C_{19}H_{38}O_6$ appears to be more likely. From the insoluble potassium salt a still smaller quantity of a solid acid was obtained which has a somewhat higher carbon content than the phellonic acid isolated by Kügler and others from cork, but which appears to be closely related to that acid.

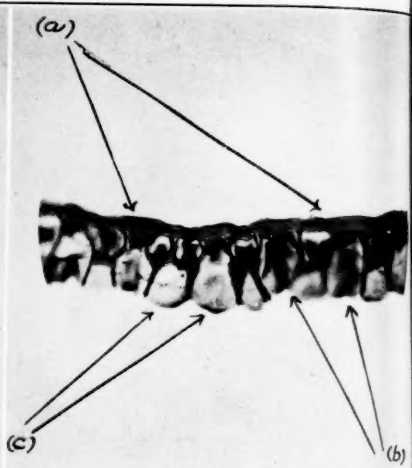
From the general description given by Frémy of his oleocutic and stearocutic acids, obtained from cuticle, it would appear that the former was a mixture of the two semi-liquid acids which we

FIG. 1.



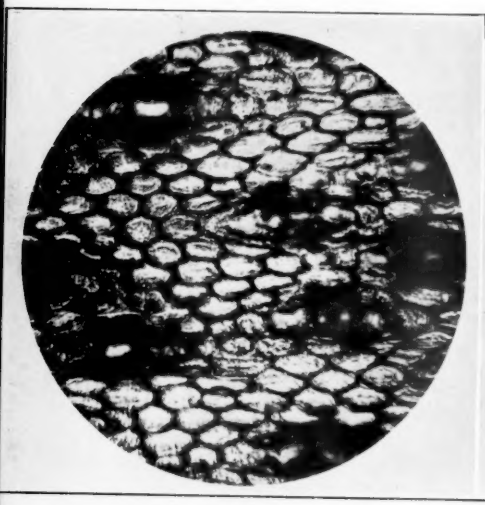
Surface view of raw cuticle from *Agave americana* showing impression of cells and stomata. (×100).

FIG 2.



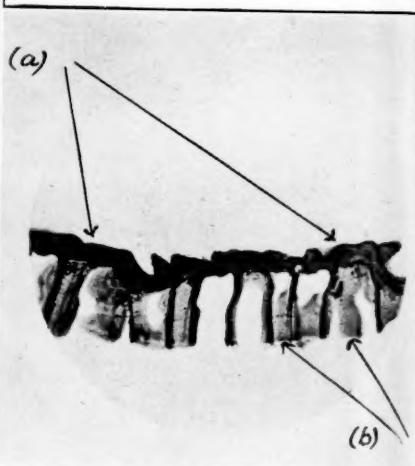
Section of raw cuticle from *Agave americana* showing :—
(*a*) Outer layer of cuticle and "teeth,"
(*b*) Dark cutinised patches,
(*c*) Cellulose membrane (×100).

FIG. 3



Surface view of purified cuticle from *Agave americana* showing structure persisting after treatment. (×100).

FIG. 4.



Section of purified cuticle from *Agave americana* showing :—
(*a*) Outer layer and "teeth" of *cutin*,
(*b*) Cutinised patches.
The cellulose membrane has been completely removed. (×100).

[*To face p.* 14

suggest should be termed cutic and cutinic acid respectively, and the latter was a mixture of phloïonic and phellonic acids.

A discussion of the results obtained on destructive distillation, and on oxidation, of cutin is reserved for a future communication, but it may be stated that on regulated distillation in a vacuum cutin yields a high proportion (60%) of tarry products, from which a hydrocarbon corresponding to pentatriacontane ($C_{35}H_{72}$) has been isolated.

Experimental.

The first supplies of cuticle were obtained from some leaves of the *Agave americana* from the Botanical Gardens, Kew. The leaves were washed with water and the outer layer of cuticle peeled off as a continuous sheet. The amount of material thus obtained was small and only served for the preliminary experiments. Subsequently, some 2000 g. of cuticle, representing the supply from 50 large leaves, were obtained from the Division of Botany, Department of Agriculture, South Africa, and it was with this material that the majority of the work was carried out.

When dry, the cuticle forms a brittle tissue, light yellow in colour, but when moistened with water it readily becomes pliable. Photomicrographs illustrating the crude material, in surface view and section, are given in Figs. 1 and 2. From the surface view it will be seen that the cuticle retains the impress of the cells which it covered and from which it has been stripped, whilst the section discloses the presence of a membrane of cellulose intimately associated with the cuticle. In Table I a number of analyses of the crude cuticle are given, the analyses for the material from the younger leaves being given first.

Table I.

Analyses of cuticle from the leaves of Agave americana.

Source.	Carbon. Per cent. on ash-free dry material.	Hydrogen.	Oxygen.	Ash. Per cent. on dry material.
Kew.....	58·6	8·9	32·5	3·7
	60·5	9·3	30·2	3·9
	62·4	9·4	28·2	2·1
South Africa.....	64·4	9·3	26·3	4·9

Extraction.—In a typical series of extractions, 300 g. of material were boiled with water in an open vessel during 3 hours and the light yellow solution was decanted off and filtered. After three such extractions the water was no longer coloured and the combined filtrates were evaporated to dryness, when they left a brown, crisp residue (yield 9 g. = 3%). By continuing the extraction in an autoclave under pressure at 140° a further quantity of extract was

obtained identical with the preceding one (yield 21 g. = 7%). This extract, although readily soluble in water once it had been isolated, was persistently retained by the cuticle and could only be completely removed after repeated extractions. The cuticle, dried at room temperature, was next extracted four or five times with absolute alcohol under reflux during 24 hours, by which time the extraction was complete. Removal of the solvent by distillation left a hard, yellow wax (yield 45 g. = 15%). Subsequent extractions with benzene and chloroform, and with alcohol under pressure, removed only traces of the material. The removal of cellulose, which forms a continuous layer on the under side of the cuticle lamella, was effected by solution in cuprammonium hydroxide. This was best carried out by suspending the cuticle in a 20% solution of ammonia containing a quantity of copper turnings and drawing a current of air through the solution. In this manner, the liquid is continually agitated and the solution of the cellulose thereby accelerated. When the ammonia solution had developed an intense blue colour, it was filtered off through glass wool, and the residual cuticle submitted to a further similar treatment. After five such treatments all the cellulose had been removed, for microchemical tests with chlor-zinc-iodide on sections of the residual material showed no trace of blue coloration. The combined filtrates were acidified with acetic acid. The flocculent, white precipitate which separated out was filtered off, thoroughly washed with hot water, and dried. On drying, the precipitate became discoloured and finally formed hard, black granules which could only be powdered with difficulty (yield 42 g. = 14%). The residue, *cutin*, after being washed with dilute hydrochloric acid and hot water and then dried, was obtained as a thin, dark-brown, elastic tissue. Photomicrographs of the cutin, in surface view and section, are shown in Figs. 3 and 4. Comparison of these with the corresponding photographs of the raw cuticle shows that, whilst the treatment with solvents has removed the cellulose membrane, the imprint of cell-structure on the cutin persists, an indication of the tough and resistant character of the material.

Examination of the Extracts.

Water-soluble Material.—The aqueous solution, which readily frothed on shaking, reduced Fehling's solution and formed a precipitate with basic lead acetate, but only produced a faint green coloration with neutral ferric chloride. Tannin material was not therefore present in any quantity. From its composition and properties the material appeared to consist principally of glucosides of the saponin type (Found: C, 48·7; H, 6·7; ash, 28·8%).

Alcohol-soluble Material.—A portion of the yellow solid was ground with purified sand and extracted in a Soxhlet successively with light petroleum, ether, acetone, and chloroform, each extraction lasting 24 hours. Light petroleum removed 28% of material, the more soluble portion of which responded to the phytosterol colour reaction. The ether-soluble portion, 53%, consisted of a mixture of free acids and saponifiable material and was not further examined (Found: C, 79·1; H, 13·1; ash, 0·8%).

Cuprammonia-soluble Material.—This extract was ground with a small quantity of concentrated sulphuric acid and poured into excess of water, making approximately a 5% acid solution. After being maintained at 90° for 12 hours, the yellow solution was filtered to remove a small quantity of insoluble material, neutralised with barium carbonate, filtered, and concentrated under reduced pressure. The yellow syrupy residue failed to crystallise when washed with small quantities of glacial acetic acid or after heating with 3% hydrochloric acid and again concentrating. When warmed with ammonium molybdate and dilute acetic acid, the residue gave the intense blue colour characteristic of fructose. The original extract boiled with concentrated hydrochloric acid strongly coloured aniline acetate paper, showing the presence of furfuraldehyde (Found: C, 44·1; H, 6·4; ash, 2·0%).

Examination of Cutin.

The composition of the residual cutin, after exhaustive treatment with the solvents previously mentioned, attained a constant value within the limits of experimental error, as shown by the following analyses on samples taken from various batches.

TABLE II.

Analyses of purified cuticle, or cutin, from the leaves of Agave americana.

Batch.	Carbon. Per cent. on ash-free dry material.	Hydrogen.	Oxygen.	Ash. Per cent. on dry material.
1	68·8	10·2	21·0	2·0
3	69·0	10·3	20·7	3·4
4	69·1	10·2	20·7	2·9

Treatment with Alcoholic Potash.—The cutin was boiled with excess of 3% alcoholic potash under reflux during 24 hours, and the dark red solution then filtered off. After four such treatments, the residue was thoroughly washed with water, dried and weighed. From three batches of cutin of 100, 150, and 300 g., the residues amounted to 7·5, 10·2, and 23·8, respectively, or approximately 7%. The composition of the residue, as shown in Table III, was

nearly constant and almost identical with that of the cutin. It follows, therefore, that the composition of the material resolved by the alcoholic potash must also approximate to this value.

TABLE III.

Analyses of cutin residues after treatment with alcoholic potash.

Batch.	Carbon. Per cent. on ash-free dry material.	Hydrogen.	Oxygen.	Ash. Per cent. on dry material.
1	67·1	8·7	24·2	31·9
3	69·1	9·8	21·1	31·3
4	68·9	9·5	21·6	31·0

From the combined alcoholic filtrates, after removal of the solvent, there was obtained a dark brown residue which readily dissolved in hot water to a clear red solution, but which on cooling became turbid and could only be filtered with difficulty. By the addition of excess of solid sodium chloride, however, a voluminous brown precipitate separated and could be filtered. The light red filtrate contained the potassium salts readily soluble in water. The residue, having been washed once with cold water, and the filtrate added to the previous one, was repeatedly boiled with water and filtered hot until a test portion of the filtrate gave no precipitate with hydrochloric acid. This solution contained the potassium salt sparingly soluble in water. The residue contained the potassium salt insoluble in water.

Acids from Potassium Salts Soluble in Water.—The filtrate was acidified with hydrochloric acid and the yellow, semi-liquid precipitate filtered off and dissolved in ether. The ethereal solution was washed, dried, and the solvent removed, leaving a brown semi-liquid mass. The corresponding potassium salts were obtained by boiling a solution of the mixed acids in absolute alcohol under reflux with excess of solid potassium carbonate until no more carbon dioxide was evolved. The cold alcoholic solution was filtered from excess of potassium carbonate, and the corresponding copper salts were obtained as a copious green precipitate by the addition of a slight excess of copper sulphate solution. The precipitate, which was insoluble in water, acetone and chloroform, was repeatedly digested with small quantities of hot absolute alcohol and filtered until the filtrate was no longer coloured. The copper salt insoluble in alcohol consisted of a light green powder, whereas the copper salt soluble in alcohol, when freed from solvent, was obtained as a dark green syrup.

The acid from the insoluble copper salt was obtained as a light brown semi-liquid mass by decomposing a chloroform suspension of the salt with hydrogen sulphide, filtering off the precipitated

copper sulphide, and evaporating the solution to dryness. It was insoluble in water and boiling light petroleum, fairly soluble in cold alcohol, chloroform, and benzene, readily so on warming (yield *ca.* 10% of the total acids obtained) (Found : C, 69·0; H, 9·9. Calc. for $C_{13}H_{22}O_3$: C, 69·0; H, 9·7%).

The *silver* salt was obtained as a copious white precipitate by the addition of a slight excess of silver nitrate to a neutral solution of the ammonium salt. When dried, it formed a dark red powder (Found : C, 45·8; H, 6·4; Ag, 31·9. $C_{13}H_{21}O_3Ag$ requires C, 46·8; H, 6·3; Ag, 32·4%).

The acid from the soluble copper salt was obtained in a similar manner by passing a stream of hydrogen sulphide through an alcoholic solution of the salt. It consisted of a yellow, semi-liquid mass and amounted to approximately 65% of the total weight of acids obtained. This acid therefore represents the chief product of saponification of cutin. Its solubility in different organic liquids was almost identical with that of the acid from the insoluble copper salt (Found : C, 68·8, 68·8; H, 10·6, 10·5; *M*, ebullioscopic in alcohol, 438, 479, 479. Calc. for $C_{26}H_{50}O_6$: C, 68·1; H, 10·9%; *M*, 458).

The *silver* salt, prepared from a neutral solution of the ammonium salt, formed a flocculent, white precipitate which darkened on drying (Found : C, 55·1; H, 8·8; Ag, 19·1. $C_{26}H_{49}O_6Ag$ requires C, 55·2; H, 8·7; Ag, 19·1%).

Acid from Potassium Salt sparingly soluble in Water.—The filtrate was acidified with hydrochloric acid and the light yellow precipitate filtered off, washed and dried. From hot chloroform it separated as a coarse, yellow, crystalline mass, m. p. 90—95°. Repeated crystallisations from this solvent failed appreciably to raise the melting point. The acid was finally purified by dissolving in boiling water, in which it was fairly soluble, and from which, after filtering and cooling, it separated as a fine, white, crystalline powder, m. p. 107—108°. Considerable loss occurred during the purification, but the yield of crude acid amounted to approximately 10% of the total acids obtained. The acid was only sparingly soluble in light petroleum, ether, or chloroform, but readily soluble in alcohol (Found : C, 62·9; H, 10·4; *M*, ebullioscopic in alcohol, 414; *M*, in camphor by Rast's method, 374. Calc. for $C_{19}H_{38}O_6$: C, 62·9; H, 10·5% *; *M*, 362).

The *silver* salt was prepared from a neutral solution of the ammonium salt and was finally dried at 110° (Found : C, 48·6; H, 8·5; Ag, 26·3. $C_{19}H_{37}O_6Ag$ requires C, 48·6; H, 7·9; Ag, 23·0%).

* For phloïonic acid, crystallised from water, Gilson gives C, 63·0; H, 9·9%.

The *ethyl* ester was prepared by saturating an alcoholic solution of the acid with dry hydrogen chloride and pouring the product into excess of water. The copious white precipitate which separated was filtered off, dissolved in ether, the ethereal solution washed, dried, and the solvent removed. The ester was readily soluble in alcohol and ether, less soluble in light petroleum and benzene. By allowing a solution of the ester in ether to evaporate spontaneously, the ester separated in rosettes of needles, m. p. 66—67° (Found: C, 66·9; H, 11·6; *M*, ebullioscopic in alcohol, 405; *M*, in camphor, 417. $C_{21}H_{42}O_6$ requires C, 64·6; H, 10·8%; *M*, 390).

Acid from Potassium Salt insoluble in Water.—The residue was suspended in dilute sulphuric acid and after some hours the flocculent, white precipitate was filtered off, washed and dried. From boiling light petroleum a flocculent, white precipitate separated on cooling, m. p. 88—90°. The small quantity obtained did not admit of further purification (Found: C, 77·4; H, 12·8%).

The separation of these four acids by fractional distillation of their methyl esters in a high vacuum was attempted, but considerable decomposition occurred during the heating and this method of separation was therefore abandoned.

Microchemical Reactions.

A number of microchemical tests were carried out in conjunction with the macrochemical work. The crude cuticle was tested for tannin by treating sections with dilute solutions of ferrous sulphate and potassium dichromate, but no coloration could be detected. Similarly, negative results were obtained by immersing sections in an alcoholic solution of phloroglucinol, washing, and subsequently treating with dilute hydrochloric acid, so that the absence of lignin can be presumed.

With solutions of chlor-zinc-iodide, or with solutions of iodine in potassium iodide after previous treatment with 70% sulphuric acid, the cuticle lamella developed a light brown colour and was sharply differentiated from the underlying layer of cellulose, which was coloured blue. After exhaustive treatment with cuprammonia in the large-scale experiments, sections of the residue showed no trace of blue colour when treated with this reagent.

In concentrated sulphuric or hydrochloric acid, the cellulose layer was rapidly destroyed, whereas the cuticle layer, even after long standing, was apparently unaltered.

With 1% solutions of Sudan III, using the method described by Lee and Priestley (*Ann. Bot.*, 1924, **38**, 528), the cuticle lamella was stained a deep red, the cellulose layer being unaffected. This

stain has recently been used in microchemical technique for the detection of fats and waxes, but it was found that the exhaustively purified cutin stained just as readily with this reagent as did the original cuticle, and, even after prolonged treatment with alcoholic potash, whereby the majority of the cutin was resolved, the residue persisted in colouring with this stain. Sudan III is a useful microchemical reagent for staining cuticle and cutin, but this fact does not appear to justify the inclusion of the latter material under the term " fat " or " wax," since cutin is quite insoluble in solvents in which fats and waxes ordinarily dissolve.

We wish gratefully to acknowledge the help we have received from the Curator, Royal Botanic Gardens, Kew, and from the Chief of the Division of Botany, Department of Agriculture, South Africa, in the supply of the material for this research. Our thanks are due also to the Safety in Mines Research Board, for whom the succeeding stages of this work are being carried out, for permission to publish this paper.

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CXCII.—*The Spatial Structure of* cyclo*Paraffins. Part I. A New Aspect of Mohr's Theory and the Isomerism of Decahydronaphthalene.*

By WILFRED ALAN WIGHTMAN.

THE recent isolation of two isomeric forms of decahydronaphthalene, which appear to stand in a *cis*- and *trans*-relationship, has definitely shown that a rigid planar conception of the structure of such compounds is no longer tenable (Hückel, *Nach. K. Ges. Wiss. Göttingen*, 1923, **43**; *Annalen*, 1925, **441**, 1). It was shown by Sachse (*Ber.*, 1890, **23**, 1363; *Z. physikal. Chem.*, 1892, **10**, 203; 1893, **11**, 185) that strain in the Baeyer sense (*i.e.*, deviation from the tetrahedral angle) can be eliminated from a non-planar structure having more than five carbon atoms in the ring, and further, that two such strain-free configurations are possible in the case of *cyclo*hexane (Fig. 1). These ideas were developed by Mohr (*J. pr. Chem.*, 1918, **98**, 315; 1922, **103**, 316), who postulated further that the temporary strain involved in a conversion of Sachse's strain-free structures one into the other is sufficiently slight to be over-

come merely by the forces due to molecular collisions. He also predicted the isomerism of decahydronaphthalene.

The principal objection to the acceptance of Sachse's structures

FIG. 1.

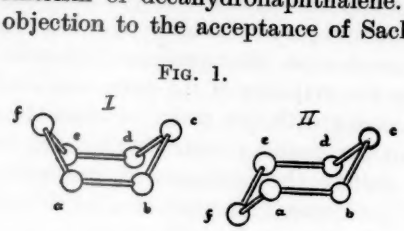


FIG. 2.

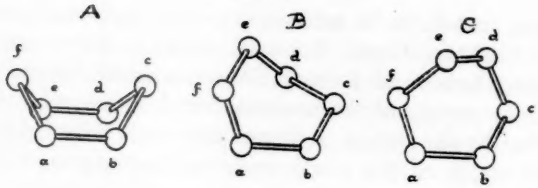
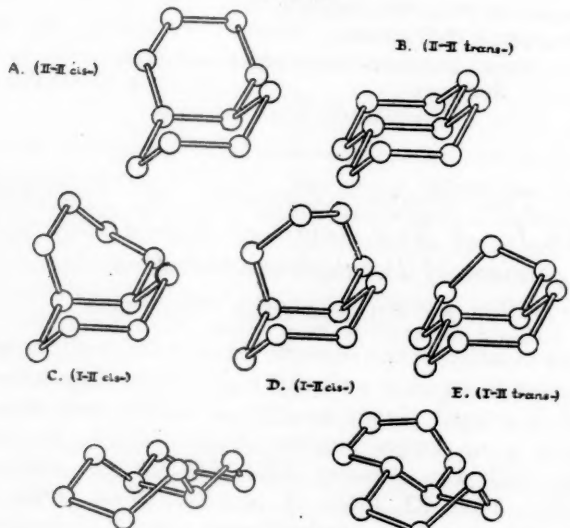


FIG. 3.



Possible isomerides of decahydronaphthalene.

as stable configurations is the large number of isomerides they would require. For whilst all the carbon atoms of type II are obviously equivalent, this is not the case with type I, and the latter, if static, requires the existence (*e.g.*) of several monosubstituted

*cyclo*hexanes. It is of interest, however, to determine whether co-ordinated relative rotations about the single bonds are possible without strain, and to examine the consequences of such a phenomenon; to this end, the author has constructed models in which these mechanical requirements are fulfilled.

The models show (*a*) that type II is a rigid structure and cannot pass into type I (or any other form) without strain, and (*b*) that type I is a "loose" structure which, although it cannot without strain be transformed into type II, is capable, by strain-free relative rotations of its carbon atoms, of passing through a series of forms which annihilate the isomeric possibilities above mentioned. Fig. 2 shows three of the configurations it can assume when the sphere (*b*) is clamped; the motion of (*a*) and (*c*) is rotatory only, whilst that of (*d*), (*e*) and (*f*) is both rotatory and translatory. If more than one sphere is fixed, the motion is completely arrested. The atoms (*c*) and (*f*) in A are equivalent to (*a*) and (*d*) in B and to (*e*) and (*b*) in C—hence the absence of isomerism. There still remains, however, the possibility of there being two *cyclo*hexanes (I and II), unless we accept Mohr's postulate.

In the case of decahydronaphthalene, Mohr showed that the theory of strain-free structures requires two isomerides incapable of interconversion by any means short of rupturing bonds. These he formulated as B and F (Fig. 3). For reasons which will presently appear, it has been thought advisable to set out all the possible combinations of pairs of the two types of strainless ring (Fig. 3). (A, C, D, and E have optical isomerides which are not shown.) All forms involving type II of the *cyclo*hexane ring are rigid: F and G are capable of strain-free rotations, but are not interconvertible —this has been confirmed by models. Inspection of the models reveals further that by applying the Mohr postulate all the *cis*-forms can be reduced to F and all the *trans*-forms to G, so that the existence of strainless motion makes no difference to the number of isomerides required by Mohr's theory.

There is one more consequence of strainless motion, however, to which attention may be directed. The effect of molecular collisions upon type I, where such motion is possible, is much less likely to cause transformation into the other type than in the case of type II, where there is no alternative. The existence of type I is therefore favoured at the expense of type II, and it seems likely that *cyclo*hexane and its derivatives may conform to type I exclusively. The existence of this type alone is sufficient to explain all the established facts and requires the existence of two (but only two) decahydronaphthalenes.

Since these ideas were developed by the author, Zelinsky (*Ber.*,

1924, **57**, 2062) has announced the isolation of a third isomeride of decahydronaphthalene. It has therefore seemed desirable to publish the above detailed examination of the isomeric possibilities of this substance, in view of the probability that the existence of more than two isomerides will lead to the abandonment of the Mohr postulate.

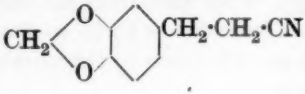
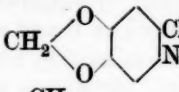
The author is indebted to Professor C. K. Ingold, F.R.S., for his interest and helpful criticism, and to Mr. Neville Warr for his aid in the design and construction of the models.

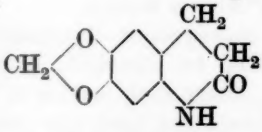
THE UNIVERSITY, LEEDS. [*Received, May 5th*, 1925.]

CXCIII.—*β-Piperonylpropionitrile and Some Derived Substances.*

By WILSON BAKER and ROBERT ROBINSON.

LAPWORTH and MCRAE (J., 1922, **121**, 1699) found that aromatic aldehydes condense with sodium cyanoacetate in aqueous solution to give excellent yields of arylidenecyanoacetic acids, and Baker and Lapworth (J., 1924, **125**, 2333) have shown that these substances may be reduced by sodium amalgam and water to saturated acids which can be decomposed with formation of β-arylpropionitriles. We have prepared by these means large quantities of β-piperonylpropionitrile (I), the transformations of which are the subject of this communication. On nitration in acetic acid solution, the nitrile yields its 6-*nitro*-derivative (II) and this is changed by reduction with tin and a mixture of acetic and hydrochloric acids into a *methylenedioxydihydrocarbostyril* (III).

(I.)  (II.) 

(III.) 

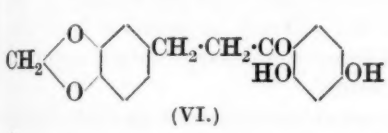
No direct synthesis of safrole has been recorded and one object of our work was to effect the transformation

$$R{\cdot}CHO \longrightarrow R{\cdot}CH_2{\cdot}CH{:}CH_2.$$

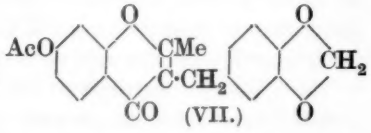
In this we were unsuccessful, but we are able to record a new synthesis of *iso*safrole. β-Piperonylpropionitrile is readily reduced by means of sodium and alcohol to *γ-piperonylpropylamine*, $CH_2O_2{:}C_6H_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$ (IV), the overall yield of this base

from piperonal being no less than 50%. From it, on treatment with methyl iodide and alcoholic sodium ethoxide, the quaternary *ammonium iodide*, $CH_2O_2{:}C_6H_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NMe_3\}I$ (V), was produced and this was transformed to the related hydroxide which it was hoped could be decomposed with formation of safrole, $CH_2O_2{:}C_6H_3{\cdot}CH_2{\cdot}CH{:}CH_2$. However, under all conditions, the product was *iso*safrole, $CH_2O_2{:}C_6H_3{\cdot}CH{:}CH{\cdot}CH_3$ (compare Senfter and Tafel, *Ber.*, 1894, **27**, 2309). The acetyl derivative of (IV) was prepared, but it was not found possible to dehydrate it to a ring homologue of 1-methyl*nor*hydrastinine (D.R.-P. 235,358) (compare Braun and Bartsch, *Ber.*, 1912, **45**, 3389).

β-Piperonylpropionitrile shows no tendency to yield a hydrindene derivative under the influence of hydrogen chloride and, under the conditions of the Hoesch synthesis, reacts with resorcinol, ultimately forming homopiperonylresacetophenone (VI). This suggested that an attempt should be made to gain further information regarding

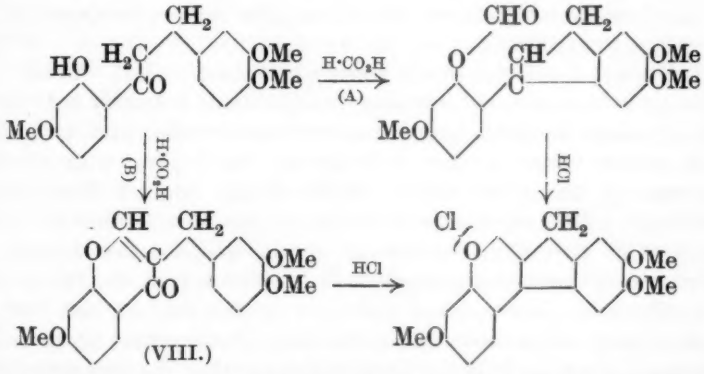


(VI.)



(VII.)

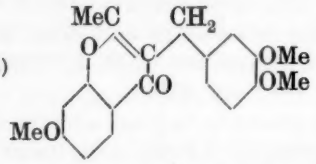
the course of the synthesis of *iso*brazilein trimethyl ether salts (Crabtree and Robinson, J., 1918, **113**, 864) by the action of boiling formic acid, in presence of zinc chloride, on homoveratrylpaeanol. Two schemes seem the most plausible, the intermediate being in (A) an indene derivative and in (B) a chromone derivative.

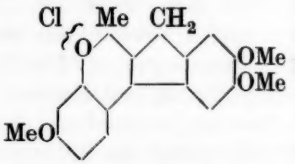


(VIII.)

Chromone derivatives of the type VIII have now been prepared, the first stage being the acetylation of the phenolic ketone (VI) by boiling acetic anhydride in presence of sodium acetate; the acetoxyhomopiperonylmethylchromone (VII) thus obtained is

hydrolysed and methylated. The whole process has been repeated starting with veratraldehyde instead of piperonal, yielding, finally, 7-methoxy-3-homoveratryl-2-methylchromone (IX). This substance shows some tendency to pass into an *iso*brazilein derivative, but its behaviour is such that it cannot possibly be regarded as an intermediate in the synthesis of the salt (X) (compare Crabtree and Robinson, *loc. cit.*).

(IX.) 



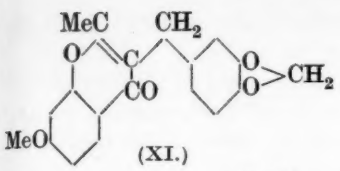
(X.)

These experiments certainly exclude scheme (B) given above and therefore favour the view that scheme (A) is correct.

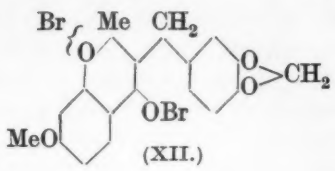
Mention should be made of the interesting dimorphism exhibited by some of these chromone derivatives, since the persistence of the phenomenon despite changes in the vicinity of position 7 in the nucleus indicates the existence of some molecular property common to the different members of the series.

Another matter of general interest encountered in the course of our work concerns a remarkable bromination mechanism. It is known that many pyrones, *e.g.*, 2 : 3-dimethylchromone (Petschek and Simonis, *Ber.*, 1913, **46**, 2014; Simonis and Elias, *Ber.*, 1915, **48**, 1499), form coloured, unstable dibromides which on boiling with water revert to the original chromone derivative and bromine. This behaviour was at first regarded as a proof of the ethylene character of pyrones, although later the dibromides were considered to be oxonium compounds.

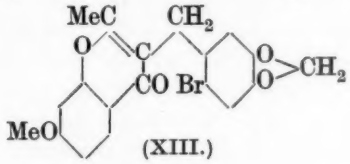
7-*Methoxy*-3-*homopiperonyl*-2-*methylchromone* (XI) forms a dibromide in acetic acid solution. The bromine is loosely held, since the substance liberates iodine from potassium iodide and, on boiling with water, some bromine is evolved. On boiling with alcohol, however, a bromo-derivative (XIII) of the original chromone is produced. This substance is stable to hot alkalis and by treatment with hydrogen bromide in acetic acid solution cannot be reconverted into the dibromide. It is obvious that the bromine in the dibromide is associated with the pyrone nucleus and that on boiling with alcohol one of the bromine atoms enters an aromatic nucleus—most likely in the position indicated. The pyrone nucleus is regarded as a dipole (Heilbron, Barnes, and Morton, J., 1923, **123**, 2564; compare Armit and Robinson, in the press) and the most acceptable formulation of the dibromides is illustrated in the expression (XII) in the particular case under discussion.



(XI.)



(XII.)



(XIII.)

Thus we conceive the reaction as an intramolecular rearrangement of the kation of a pyrylium bromide. It is favoured by the polarising effect of the chromone dipole on the bromine and by the proximity in space of a bromine atom, which has a tendency to separate with a positive charge, to an unsaturated centre which has a tendency to acquire a negative charge.

Experimental.

β-*Piperonylpropionitrile* (I) was obtained from α-cyano-β-piperonylpropionic acid (Piccinini, *Atti R. Accad. Sci. Torino*, 1904, **39**, 121; Baker and Lapworth, *loc. cit.*) by thermal decomposition in presence of copper powder (compare Willstätter and Pummerer, *Ber.*, 1904, **37**, 3745; Rinkes, *Rec. trav. chim.*, 1920, **39**, 205). The acid (45 g.) and washed copper bronze (10 g.) were rapidly heated over a free flame in a distilling flask of about 250 c.c. capacity. A very lively evolution of gas set in and ceased suddenly in about a minute. A further quantity (45 g.) of the acid was introduced and this also decomposed and the resulting nitrile distilled. A colourless oil (50 g.), b. p. 186—187°/18—20 mm., and a pale yellow, higher-boiling fraction (6 g.) were obtained. After several months a sample crystallised at once when it was disturbed. The substance may be obtained in large, well-developed prisms, m. p. 33°, by adding light petroleum to a concentrated ethereal solution (Found : C, 68·7; H, 5·2; N, 8·1. $C_{10}H_9O_2N$ requires C, 68·5; H, 5·2; N, 8·0%). The nitrile is readily soluble in most organic solvents and dissolves in sulphuric acid to a deep crimson solution which, when diluted with a little water and gently heated, becomes olive-green. By treatment with a warm alkaline solution of hydrogen peroxide (Radziszewski, *Ber.*, 1885, **18**, 355) it was readily converted into the known β-piperonylpropionamide, m. p. 123·5° (Decker, *Annalen*, 1913, **395**, 289; Borsche and Eberlein, *Ber.*, 1914, **47**, 1469), which was also isolated as the result of an experiment made with the object

of closing the hydrindene ring by acting on the nitrile in dry ethereal solution with hydrogen chloride.

β-6-*Nitropiperonylpropionitrile* (II) was obtained by addition of nitric acid (1 c.c.; *d* 1·42) to a solution of β-piperonylpropionitrile (2·5 g.) in acetic acid (25 c.c.). After 15 minutes, the mixture was added to water (200 c.c.) and the crystals (2·3 g.) were collected; they crystallised from alcohol in pale honey-coloured, flat needles, m. p. 113° (Found: C, 54·5; H, 3·7; N, 12·9. $C_{10}H_8O_4N_2$ requires C, 54·5; H, 3·7; N, 12·7%). On heating with dilute aqueous sodium hydroxide, ammonia is evolved and a deep crimson solution produced. The methylenedioxy-group is hydrolysed in all probability, since the product gives an olive-green coloration with ferric chloride. There was also evidence of an attack on the methylenedioxy-group during the course of acid hydrolysis. A mixture of β-6-nitropiperonylpropionitrile (2 g.) and concentrated hydrochloric acid (100 c.c.) was boiled for 18 hours. On cooling, the filtered solution deposited yellow plates (0·9 g.) which, after crystallisation from alcohol, had m. p. 153—153·5° (Found: C, 50·2; H, 4·0; N, 6·0. $C_{10}H_9O_6N$ requires C, 50·2; H, 3·8; N, 5·9%). This substance is therefore β-6-*nitropiperonylpropionic acid*. The mother-liquors from several preparations were concentrated to a small bulk, filtered from some of the acid just described, and extracted with ether. The yellow, crystalline residue, left on removal of the solvent, gave an olive-green colour with ferric chloride and appeared to be a mixture containing about 60% of a catechol derivative. β-6-Nitropiperonylpropionitrile (3 g.) was dissolved in warm acetic acid (45 c.c.), and tin (10 g.) and concentrated hydrochloric acid (10 c.c.) were added; after 12 hours, hydrochloric acid (5 c.c.) was introduced and the mixture heated on the steam-bath until the reaction was complete. The tin was eliminated as sulphide from the hot, diluted solution, and the acetic acid by boiling. The neutralised solution deposited small crystals (1·3 g.) and the substance was recrystallised from alcohol (charcoal) in colourless plates which softened at 227° and melted at 230° (Found: C, 62·9; H, 4·8; N, 7·5. Calc., for $C_{10}H_9O_3N$, C, 62·8; H, 4·8; N, 7·3%). The substance has feebly basic properties and appears to be identical with the ethylamidopiperonyl-ω-carboxylic anhydride, m. p. 235° with slight previous softening, prepared by F. M. Perkin (J., 1891, **59**, 159) by reduction of ethyl 6-nitropiperonylacrylate. The latter compound can be obtained from 6-nitropiperonal, a fact which establishes the orientation of the substituents.

γ-*Piperonylpropylamine* (IV).—In the course of 2 hours, sodium (35 g.) was added in small pieces to a boiling solution of β-piperonylpropionitrile (17·5 g.) in absolute alcohol (350 c.c.). Water

(2 l.) was added and the base extracted with ether, the dried solution being distilled. 15·3 G. of a colourless liquid, b. p. 160—161°/14 mm., were obtained (yield 85%).

γ-Piperonylpropylamine is a highly refracting liquid, $d_{16°}^{16°}$ 1·141, having a weak basic odour. It is sufficiently soluble in water to impart a strong alkaline reaction and on exposure to air gives a solid *carbonate*, m. p. 92—94°. The *hydrochloride* crystallises from alcohol in long, colourless, silky needles, m. p. 206—208° (Found: C, 55·8; H, 6·7; N, 6·5; Cl, 16·3. $C_{10}H_{14}O_2NCl$ requires C, 55·7; H, 6·6; N, 6·5; Cl, 16·4%). The *acetyl* derivative,

$$CH_2O_2{:}C_6H_3{\cdot}[CH_2]_3{\cdot}NH{\cdot}COMe,$$

obtained by the action of acetic anhydride on the base, crystallises from water or from benzene in colourless needles, m. p. 89° (Found: N, 6·4. $C_{12}H_{15}O_3N$ requires N, 6·3%).

Piperonylidene-γ-piperonylpropylamine,

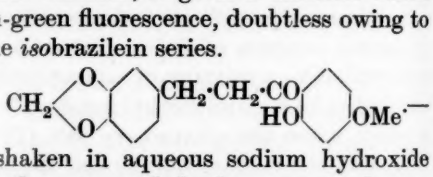
$$CH_2O_2{:}C_6H_3{\cdot}[CH_2]_3{\cdot}N{:}CH{\cdot}C_6H_3{:}O_2CH_2,$$

was prepared by heating a mixture of the amine (5 g.) and piperonal (4·2 g.) on the steam-bath for 30 minutes. The crystalline mass obtained on cooling was dissolved in warm acetone; the filtered solution deposited colourless, glistening plates, m. p. 79·5° (Found: N, 4·5. $C_{18}H_{17}O_4N$ requires N, 4·5%). The derivative is readily soluble in organic solvents with the exception of light petroleum.

γ-*Piperonylpropyltrimethylammonium Iodide* (V).—A freshly-prepared solution of sodium ethoxide (2 mols.) in alcohol (45 c.c.) was added to a mixture of γ-piperonylpropylamine (10 g.; 1 mol.), alcohol (25 c.c.), and methyl iodide (15 c.c.), and the whole was gently heated, when the quaternary salt (13 g.) crystallised. Ether was added to the mother-liquor, and the mixture of sodium iodide and the quaternary ammonium iodide which separated was collected. On standing in the air, the former deliquesced, leaving the latter unchanged (2 g.). The *iodide* crystallises from alcohol in colourless, shining plates, m. p. 146° (Found: I, 36·4. $C_{13}H_{20}O_2NI$ requires I, 36·4%). The iodide (10 g.) was converted into hydroxide by means of an excess of freshly precipitated silver oxide in presence of water (50 c.c.), the strongly alkaline filtrate was concentrated on the steam-bath under diminished pressure, and the syrupy residue was decomposed by gradually raising the temperature to 160°, water, trimethylamine, and a little *iso*safrole being carried over. The distillate and residue were combined, acidified with dilute sulphuric acid, and distilled in steam. The oil was collected from the distillate by ether, and 2·77 g. of *iso*safrole were obtained. The yield from the iodide is 60% and the overall yield from piperonal is 24%. The substance was identified by its b. p. and characteristic picrate,

red needles, m. p. 73·5—74° (Found : N, 10·9. Calc. for $C_{16}H_{13}O_9N_3$, N, 10·8%) as ordinary *trans-iso*safrole. The m. p. of the picrate was not depressed by admixture with an authentic specimen (compare Hoering and Baum, *Ber.*, 1909, **42**, 3076; Nagai, *J. Coll. Eng. Tokyo Imp. Univ.*, 1921, **11**, 83 in reference to isomeric *iso*safroles).

Homopiperonylresacetophenone (VI).—A solution of β-piperonylpropionitrile (20 g.) and resorcinol (25 g.) in dry ether (80 c.c.) was saturated at 0° with hydrogen chloride and kept at 0° for 48 hours, ether (50 c.c.) being added when half this time had elapsed. The ketimine hydrochloride separated as a yellow, crystalline crust, which was washed with ether and decomposed by heating with water during 30 minutes on the steam-bath. The *ketone* crystallised on standing and was crushed, washed, and dried (15·8 g.). The ethereal mother-liquor deposited a fresh crop of ketimine hydrochloride on dilution with fresh ether, and the ketone from this was purified by solution in aqueous sodium hydroxide, a further 4 g. being ultimately isolated. The substance crystallises from hot aqueous methyl alcohol in colourless, shining plates, m. p. 130° (Found : C, 67·1; H, 5·0. $C_{16}H_{14}O_5$ requires C, 67·1; H, 4·9%). Homopiperonylresacetophenone is readily soluble in ether, the simple alcohols, and benzene, and dissolves to some extent in hot water. When heated with acetic anhydride and zinc chloride, it gives a solution which exhibits an intense, yellowish-green fluorescence, doubtless owing to the production of a salt of the *iso*brazilein series.

Homopiperonylpaeanol,* 

The foregoing phenol was shaken in aqueous sodium hydroxide with methyl sulphate, when the *monomethyl* ether separated even from the alkaline solution. The substance crystallises from methyl alcohol in colourless needles, m. p. 89—90° (Found : C, 67·9; H, 5·4. $C_{17}H_{16}O_5$ requires C, 68·0; H, 5·4%). The phenolic function is very weak (compare the case of benzylpaeanol; Crabtree and Robinson, *loc. cit.*), although an alcoholic solution develops a reddish-violet coloration with ferric chloride. When heated with acetic anhydride and zinc chloride, it gives a red solution exhibiting intense ivy-green fluorescence. No chromone derivative could be obtained by the action of acetic anhydride and sodium acetate on the substance. It appears to be a general rule that paeanol derivatives cannot be converted into chromones by acetic anhydride, whereas the corresponding resacetophenones undergo the reaction

* Tognazzi (*Gazzetta*, 1924, **54**, 697) has obtained this substance by the catalytic reduction of piperonylidenepaeanol. The m. p. quoted is 85—87°.

(as shown below in the present instance) smoothly and often with the production of excellent yields.

7-*Hydroxy*-3-*homopiperonyl*-2-*methylchromone* (corresponding with VII).—The acetyl derivative described below (5 g.) was hydrolysed by boiling dilute aqueous sodium carbonate until solution occurred (2·5 hours), and the filtered solution was acidified with hydrochloric acid. The colourless, crystalline precipitate was dried (4·07 g.), and recrystallised from ethyl alcohol, separating in small, colourless, silky needles (Found : C, 69·4; H, 4·7. $C_{18}H_{14}O_5$ requires C, 69·7; H, 4·6%). The solution in aqueous or alcoholic sodium hydroxide exhibits a bluish-violet fluorescence. Prepared as described, the substance is obtained in the α-form, m. p. 214—215°, then solidifying, and melting at 222—223° (β-form). The α-form was obtained from either modification of the acetyl derivative, but on one occasion the pasty mass of needle crystals of the α-variety changed to small, well-formed prisms. These consisted of the β-form, m. p. 222—223°, and could be recrystallised unchanged from alcohol. A mixture of both forms melted at 222—223°. If a hot alcoholic solution of the α-form is seeded with the β-form, slow crystallisation gives the pure β-form, but rapid cooling causes the separation of a mixture.

The *acetyl* derivative (VII) was obtained in excellent yield when a mixture of homopiperonylresacetophenone (5 g.), anhydrous sodium acetate (5 g.), and acetic anhydride (20 c.c.) was heated at 180° for 15 hours. The solid (6·2 g.) obtained by decomposition with dilute hydrochloric acid crystallised from alcohol containing a little water in colourless needles, m. p. 101·5° (Found : C, 68·3; H, 4·4. $C_{20}H_{16}O_6$ requires C, 68·2; H, 4·6%). The yield of hydroxyhomopiperonylmethylchromone from homopiperonylresacetophenone is 93% of that theoretically possible. This acetyl derivative also is dimorphous and the relation between the two forms resembles that existing between those of the related phenol. The modification directly obtained is the α-form, and this solidifies almost immediately after melting and then melts at 119·5°. As before, this β-variety is the more stable and transformation of the supercooled compound into the α-form could not be accomplished by seeding, although the change from α to β could readily be brought about. In one case only, the β-form was obtained directly from the preparation and had m. p. 119·5°, unaltered by crystallisation. Both varieties crystallise in needles and the change β to α has not been observed.

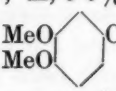
The *methyl* ether (XI), obtained by shaking the phenol dissolved in alcoholic potassium hydroxide with methyl sulphate, crystallised from methyl alcohol in small, colourless prisms, m. p. 124—125°

(Found : C, 70·0; H, 5·1. $C_{19}H_{16}O_5$ requires C, 70·3; H, 5·0%). Under a great variety of conditions this substance can be made to yield fluorescent solutions by treatment with powerful acid condensing agents, but it was found impossible to isolate any tangible quantities of definite oxonium salts of the *iso*brazilein type. The greater part of the material was always converted into insoluble, pink solids which could not be crystallised.

Dibromide of the Methyl Ether (XII).—7-Methoxy-3-homopiperonyl-2-methylchromone (2 g.; 1 mol.) dissolved in acetic acid (20 c.c.) was treated with a 10% acetic acid solution of bromine (1 mol.), when yellow crystals at once began to separate; after 30 minutes, these were collected, washed with acetic acid, and dried (2·8 g.; 93%) (Found : Br, 33·1. $C_{19}H_{16}O_5Br_2$ requires Br, 33·1%). The ochre-yellow powder becomes orange on keeping, and on boiling with acetic acid a pink solution with green fluorescence is produced. The melting point is indefinite; darkening commences at about 155°, and at about 167° the substance is almost black and softens, finally melting to a deep red liquid above 170°. The solution in sulphuric acid is reddish-purple, but rapidly becomes brown, grey, olive-green and then brown again. On boiling the dibromide (1 g.) with alcohol (100 c.c.) for 30 minutes, a pink, faintly fluorescent solution is produced and, on cooling, this deposits faintly pink, small needles (0·72 g.), m. p. 206—207° (Found : C, 56·6; H, 3·9; Br, 19·7. $C_{19}H_{15}O_5Br$ requires C, 56·6; H, 3·8; Br19·8%). This substance, probably XIII, is stable to hot alcoholic potassium hydroxide for a short time and when heated with zinc chloride and acetic anhydride gives a carmine solution with intense yellowish-green fluorescence. Cyclisation by treatment with activated magnesium in dry *iso*amyl-ethereal solution could not be effected.

α-*Cyano*-β-*veratrylacrylic acid* was obtained from veratraldehyde in quantitative yield by an application of the method of Lapworth and McRae (*loc. cit.*). The pale yellow needles obtained on acidification of the solution were dried, and crystallised from hot water or from ethyl alcohol in thin, pale yellow, microscopic needles, m. p. 201—202° (Found : C, 61·4; H, 4·8; equiv., 232·3. $C_{12}H_{11}O_4N$ requires C, 61·8; H, 4·8%; equiv., 233·1). The acid crystallises from methyl alcohol in lustrous, long needles of a greyish-violet colour and having a metallic appearance. The substance contains solvent of crystallisation (Found : equiv., 264·3. $C_{12}H_{11}O_4N,CH_4O$ requires equiv., 265·2) and on exposure to the air the crystals become opaque, yellow, and friable. The peculiar appearance is due to fluorescence and it may be noted that the related ethyl ester exhibits blue fluorescence in the crystalline state (Kauffmann, *Ber.*, 1919, **52**, 1422).

α-*Cyano*-β-*veratrylpropionic Acid.*—The reduction of the acrylic acid was carried out as described by Baker and Lapworth (*loc. cit.*), the weight of the saturated acid obtained being equal to that of the original veratraldehyde. It crystallised from benzene in bunches of needles, m. p. 139° (Found: C, 61·1; H, 5·5; equiv., 236·3. $C_{12}H_{13}O_4N$ requires C, 61·3; H, 5·6%; equiv., 235·1).

β-*Veratrylpropionitrile*,  .—This substance and all those described below were obtained by the methods already recorded for the piperonyl analogues. The nitrile was obtained in 70% yield as a very pale yellow oil, b. p. 194—195°/17 mm., which crystallised and could be recrystallised from ether–ligroin in colourless prisms, m. p. 46·5° (Found: C, 68·9; H, 6·8. $C_{11}H_{13}O_2N$ requires C, 69·1; H, 6·9%).

Homoveratrylresacetophenone, obtained in poor yield (22%), crystallised from methyl alcohol, in which it was sparingly soluble, in colourless needles, m. p. 146—147° (Found: C, 67·2; H, 5·9. $C_{17}H_{18}O_5$ requires C, 67·5; H, 6·0%).

7-*Acetoxy*-3-*homoveratryl*-2 *methylchromone* separates from ethyl alcohol in colourless, tabular parallelipipeda, m. p. 140·5° (Found: C, 68·4; H, 5·5. $C_{21}H_{20}O_6$ requires C, 68·5; H, 5·5%).

7-*Hydroxy*-3-*homoveratryl*-2-*methylchromone*, obtained in 90% yield from homoveratrylresacetophenone, crystallises from hot, aqueous ethyl alcohol in small, glistening plates, m. p. 183—184° (Found: C, 69·8; H, 5·6. $C_{19}H_{18}O_5$ requires C, 69·9; H, 5·6%). The alkaline solutions of this chromone exhibit blue fluorescence.

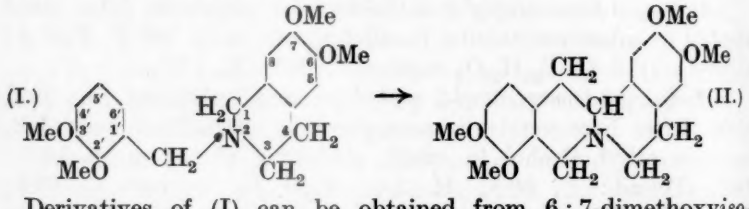
7-*Methoxy*-3-*homoveratryl*-2-*methylchromone* (IX) separates from methyl alcohol in colourless, obliquely truncated, four-sided prisms, m. p. 108° (Found: C, 70·3; H, 5·8. $C_{20}H_{20}O_5$ requires C, 70·5; H, 5·9%). This substance was prepared because it was thought that formaldehyde from the methylenedioxy-group might vitiate the results of experiments on the condensation of the piperonyl analogue. When it was boiled with acetic anhydride and zinc chloride, there was evidence that some *iso*brazilein derivative was produced, but the yield was very small.

THE UNIVERSITY, MANCHESTER. [*Received, April 6th*, 1925.]

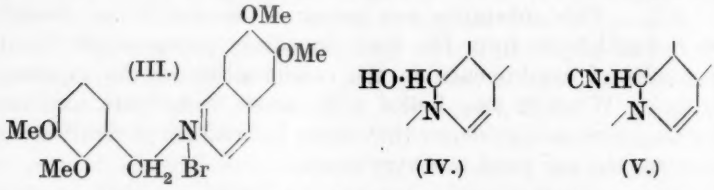
CXCIV.—*Synthetical Experiments in the* iso*Quinoline Group. Part I.*

By ROBERT DOWNS HAWORTH and WILLIAM HENRY PERKIN, jun.

IN the course of experiments on the constitution and synthesis of the berberine alkaloids, which have occupied much of the attention of these laboratories during the last few years, a large number of new derivatives of *iso*quinoline have been prepared which were not included in the previous publications, partly in order to economise space and partly because they did not lead directly to the synthesis of these alkaloids or their derivatives. Since, however, these new substances have an interest of their own and may very probably prove to be useful in other synthetical work, we have decided to publish a brief account of their preparation and properties. The first of these papers had for its central idea the synthesis of berberine alkaloids from 6 : 7 : 2′ : 3′-*tetramethoxy*-2-*benzyl*-1 : 2 : 3 : 4-*tetrahydro*iso*quinoline* (I) derivatives by the introduction of a carbon atom between the positions 1 and 6′, thus :

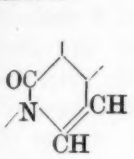


Derivatives of (I) can be obtained from 6 : 7-dimethoxy*iso*quinoline and 2 : 3-dimethoxybenzyl bromide, which readily combine to give the iso*quinolinium bromide* (III), from which the corresponding *ψ-base* (IV), *ψ*-cyanide (V), iso*quinolone* (VI), and *tetrahydro*iso*quinoline* (I) have been prepared. Several attempts have



been made to convert 6 : 7 : 2′ : 3′-tetramethoxy-2-benzyl-1 : 2 : 3 : 4-tetrahydro*iso*quinoline (I) into the berberine type (II), but without success. Thus methylal and acetal had no action on the tetrahydro*iso*quinoline and, although Schneider and Schröter (*Ber.*, 1920, **53**, 1459) have shown that sulphoacetic acid converts papaverine into coralyne (VII), it does not react with the tetrahydro*iso*quinoline (I). The substance (I) was next oxidised

to the *dihydro*isoquinolinium *iodide* (VIII), from which the corresponding *ψ-base* (IX), *ψ-cyanide* (X) and iso*quinolone* (XI) have been obtained.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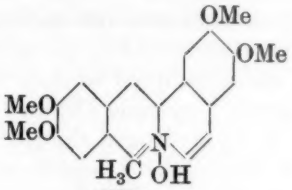
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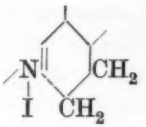
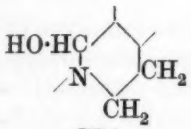

(VIII.)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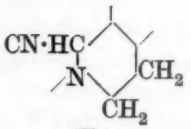
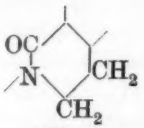
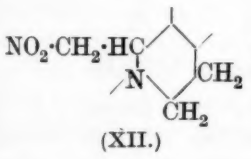
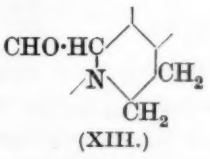

(X.)


(XI.)

The remaining stages of the research had for their object the conversion of the substances (VIII–XI) into the corresponding 1-aldehydo- or 1-carboxy-tetrahydro*iso*quinoline derivatives, as it seemed likely that these might be useful in synthesising the required berberine or corydaline structure. The first method investigated depends on the fact that, as was first shown by Hope and Robinson (J., 1911, **99**, 2114), *ψ*-bases condense with aliphatic nitro-compounds, and we found that the *ψ*-base (IX) readily yields a nitromethyl derivative (XII) on treatment with nitromethane. It was hoped that reduction of this derivative would lead to the formation of an oxime and that the aldehyde (XIII), obtained from this, would readily lose water, giving a substance (XIV) of the dihydroberberine type.


(XII.)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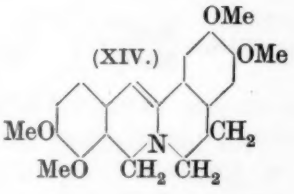
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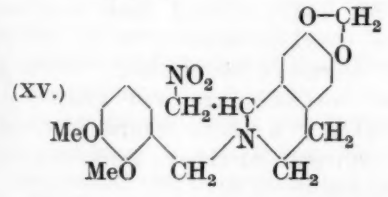
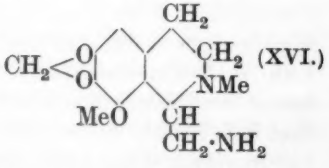

(XV.)

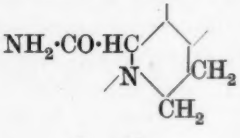

(XVI.)

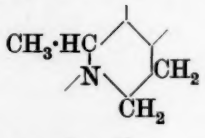
All experiments in this direction have been unsuccessful owing to the elimination of methylamine during reduction and formation

of the ψ-base (IX), and it was also observed that 6 : 7-*methylenedioxy*-2′ : 3′ - *dimethoxy* - 2 - *benzyl* - 1 - *nitromethyl* - 1 : 2 : 3 : 4-*tetrahydroisoquinoline* (XV) behaves similarly towards reducing agents. On the other hand, anhydrocotarnine-nitromethane was reduced to anhydrocotarnine-methylamine (XVI) in both acid and alkaline solutions. We have also attempted to close the ring with the aid of the cyano-group of the ψ-cyanide (X) and the hydrogen of the 6-position by means of dry hydrogen chloride, but, in spite of the careful exclusion of moisture, the ψ-cyanide was always, to a large extent, converted into the corresponding quaternary ammonium salt and no internal condensation took place.

In some cases, partial hydrolysis occurred with formation of small quantities of *tetramethoxybenzyltetrahydroisoquinolinecarboxylamide* (XVII). Other experiments showed that the instability of the ψ-cyanide is so pronounced that it is unsuitable for synthetical purposes and attempts to oxidise it to the more stable 1-cyano*iso*quinolinium iodide were unsuccessful. Again, although the ψ-cyanide (X) reacts with magnesium methyl iodide with the formation of *tetramethoxybenzylmethyltetrahydroisoquinoline* (XVIII), the attempt to oxidise this base to the corresponding dihydro*iso*quinolinium iodide led only to the formation of an uninviting substance, which showed no sign of possessing a reactive methyl group capable of condensing with nitrosodimethylaniline or of conversion into the aldehydo-group by other means.

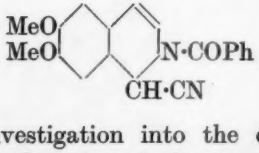
(XVII.)

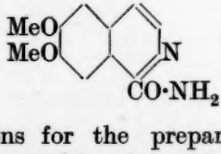




(XVIII.)

(XIX.)





(XX.)

An investigation into the conditions for the preparation of 6 : 7-dimethoxy*iso*quinoline-1-carboxylic acid has led to interesting results. Reissert (*Ber.*, 1905, **38**, 3427) showed that 1-cyano-2-benzoyl-1 : 2-dihydro*iso*quinoline could be obtained by the action of potassium cyanide and benzoyl chloride on *iso*quinoline. Starting with 6 : 7-dimethoxy*iso*quinoline, we have prepared *dimethoxycyanobenzoyldihydroisoquinoline* (XIX) in a similar manner and find that it is readily hydrolysed by hydrogen chloride to benzaldehyde and dimethoxy*iso*quinolinecarboxylamide (XX).

This amide condenses with 2 : 3-dimethoxybenzyl bromide, and the product, on reduction, yields an acid amide which is identical

with the amide (XVII) obtained by the action of hydrogen chloride on the ψ-cyanide (X).

This amide could, however, not be hydrolysed to the corresponding acid, and, unfortunately, we have failed to find a method for condensing the $-CO\cdot NH_2$ group of the amide with the hydrogen atom in the 6′-position which would have resulted in a substance containing the berberine structure.

EXPERIMENTAL.

The 2 : 3-dimethoxybenzaldehyde used in the following experiments was prepared by the methylation of *o*-vanillin by means of methyl sulphate and methyl-alcoholic potassium hydroxide. During the preparation of large quantities of this substance, a small quantity of an oil was isolated which was insoluble in sodium hydrogen sulphite and yielded 2 : 3-dimethoxybenzaldehyde on warming with dilute acids. This oil distilled at 134—136°/11 mm. and proved to be 2 : 3-*dimethoxybenzaldehyde dimethylacetal*, $(MeO)_2C_6H_3\cdot CH(OMe)_2$ (Found : C, 62·3; H, 7·6. $C_{11}H_{16}O_4$ requires C, 62·3; H, 7·5%). 2 : 3-Dimethoxybenzyl alcohol was prepared from the aldehyde by the action of alcoholic potassium hydroxide under the conditions described by Doutteau (*Bull. Soc. chim.*, 1912, **11**, 653).

2 : 3-*Dimethoxybenzyl bromide* was obtained by dissolving the alcohol (30 g.) in dry benzene (250 c.c.), cooling in a freezing mixture, and saturating with hydrogen bromide. The excess of hydrogen bromide was removed by calcium carbonate, the whole filtered, the residue washed with benzene, the filtrate and washings were dried over potassium carbonate, the benzene was removed, and the residue rapidly distilled under reduced pressure.

This distillation is necessary in order to free the bromide from a dark coloured impurity. The distillate solidified on cooling and melted at about 27—29° (Found : Br, 34·0. $C_9H_{11}O_2Br$ requires Br, 34·6%).

This bromide possesses very powerful lachrymatory properties and produces violent sneezing. It dissolves in the usual solvents and slowly undergoes hydrolysis in the presence of moist air.

6 : 7 : 2′ : 3′-*Tetramethoxy-2-benzyliso*quinolinium *Bromide* (III).—The 6 : 7-dimethoxy*iso*quinoline employed in this research was obtained by the fusion of xanthaline with potassium hydroxide under the conditions described by Dobson and Perkin (J., 1911, **99**, 137). This substance (9 g.) and 2 : 3-dimethoxybenzyl bromide (11 g.) were allowed to react in dry benzene (50 c.c.), and after remaining over-night, the iso*quinolinium bromide* was collected and washed with benzene, when an almost quantitative yield was obtained (Found : C, 57·4; H, 5·2; Br, 19·0. $C_{20}H_{22}O_4NBr$ requires C, 57·1;

H, 5·2; Br, 19·0%). This bromide is readily soluble in water, ethyl and methyl alcohols, and acetone, but sparingly soluble in ether or benzene. It separates from ether–alcohol in long, colourless needles which soften at 109° and melt to a pale yellow liquid at 114°. When a crystal is dissolved in concentrated sulphuric acid, bromine is liberated, the solution becomes colourless on warming, and the addition of a drop of nitric acid produces a blood-red coloration. The corresponding *iodide* is precipitated when potassium iodide is added to an aqueous solution of the bromide and separates from methyl alcohol in large, colourless, rhombic prisms, m. p. 204—205° (Found : I, 27·0. $C_{20}H_{22}O_4NI$ requires I, 27·2%). On addition of iodine in potassium iodide to the aqueous solution of the bromide (III), a *periodide* is precipitated which separates from alcohol in slender, green needles, m. p. 159—160°. When this is shaken with dilute sulphurous acid, it is converted into the *iso*quinolinium iodide.

1-*Hydroxy*-6 : 7 : 2′ : 3′-*tetramethoxy*-2-*benzyl*-1 : 2-*dihydro*iso-*quinoline* (IV).—When a large excess of sodium hydroxide was added to the aqueous solution of the bromide (III), the ψ-base (IV) slowly separated as a thick, gelatinous precipitate which was collected, washed with water, and dried in an evacuated desiccator (Found : C, 67·0; H, 6·6. $C_{20}H_{23}O_5N$ requires C, 67·2; H, 6·4%). This ψ-base is a colourless, amorphous substance readily soluble in dilute acids and is reprecipitated by sodium hydroxide but not by ammonia or potassium acetate. It is readily soluble in the usual organic solvents, and solutions in alcohol or benzene undergo oxidation to the corresponding *iso*quinolone (VI) on exposure to air. The colourless solution of the ψ-base in concentrated sulphuric acid becomes blood-red on the addition of a drop of nitric acid.

A *stannous chloride* derivative is precipitated on adding a solution of stannous chloride to the solution of the ψ-base in dilute hydrochloric acid. It crystallises from water in elongated prisms, m. p. 163—164°, and yields the amorphous ψ-base on decomposition by hydrogen sulphide.

1-*Cyano*-6 : 7 : 2′ : 3′-*tetramethoxy*-2-*benzyl*-1 : 2-*dihydro*iso-*quinoline* (V).—When a concentrated solution of potassium cyanide was added to an aqueous solution of the *iso*quinolinium bromide (III), the *ψ-cyanide* (V) separated as an oil which rapidly solidified. This, after being thoroughly dried in an evacuated desiccator, separated from benzene in small needles, m. p. 120—122° (Found : N, 7·7. $C_{21}H_{22}O_4N_2$ requires N, 7·6%).

This ψ-cyanide is soluble in alcohol, chloroform, or nitrobenzene, but sparingly soluble in benzene or petroleum. It dissolves with decomposition in water and is reprecipitated on the addition of

potassium cyanide. It rapidly loses hydrogen cyanide in the presence of moisture or dilute acids.

6 : 7 : 2′ : 3′-*Tetramethoxy*-2-*benzyl*-1-iso*quinolone* (VI).—(i) The *iso*quinolinium bromide (III ; 2 g.) was dissolved in water (40 c.c.) and potassium hydroxide (1 g.), and the solution oxidised by potassium ferricyanide (4·5 g.) in water (20 c.c.). After boiling for a few minutes, the mixture was cooled, when the *iso*quinolone separated in almost theoretical yield. (ii) The *iso*quinolinium bromide (III; 2 g.), dissolved in alcohol (15 c.c.), was boiled for ½ hour with a 50% solution of potassium hydroxide (10 c.c.). Most of the alcohol was removed by distillation, the residue diluted with water, and the crude brown *iso*quinolone recrystallised from methyl alcohol. This *iso*quinolone separates from methyl alcohol in colourless prisms, m. p. 171°. It is slightly soluble in ether, benzene, or alcohol in the cold, readily soluble in hot alcohol or benzene, and is a weak base, dissolving in glacial acetic acid or concentrated mineral acids and being reprecipitated on dilution with water (Found : C, 67·5; H, 5·9; N, 3·8. $C_{20}H_{21}O_5N$ requires C, 67·6; H, 5·9; N, 3·9%).

6 : 7 : 2′ : 3′-*Tetramethoxy*-2-*benzyl*-1 : 2 : 3 : 4-*tetrahydro*iso-*quinoline* (I).—The bromide (III; 5 g.), dissolved in alcohol (150 c.c.) and concentrated hydrochloric acid (150 c.c.), was boiled with a large excess of granulated tin for 6 hours. Most of the alcohol was removed by distillation under reduced pressure, and the residual liquid decanted into water (4 vols.), when a tin double salt separated which was collected and decomposed by hydrogen sulphide. The filtrate from the tin sulphide was concentrated and sodium hydroxide added, when the *tetrahydroisoquinoline* separated as an oil which rapidly solidified (3 g.) (Found : C, 69·6; H, 7·3. $C_{20}H_{25}O_4N$ requires C, 69·9; H, 7·3%).

This tetrahydro*iso*quinoline is readily soluble in benzene, chloroform, or acetone, sparingly soluble in ether or petroleum, and crystallises from methyl alcohol in colourless prisms, m. p. 112—113°. The solution in concentrated sulphuric acid becomes blood-red on the addition of a drop of nitric acid.

The *stannous chloride* derivative separates from hot water in small plates, m. p. 109—110°. The base was recovered after heating for an hour with methylal or acetal and also after heating with sulphoacetic acid under the conditions employed by Schneider and Schröter (*loc. cit.*).

6 : 7 : 2′ : 3′-*Tetramethoxy*-2-*benzyl*-3 : 4-*dihydroisoquinolinium Iodide* (VIII).—The tetrahydro*iso*quinoline (I; 2·5 g.) was dissolved in alcohol (25 c.c.) containing potassium acetate (1 g.), and the solution boiled during the gradual addition of a 10% solution of iodine in alcohol (18 c.c.). Most of the alcohol was removed by

distillation, and the residue treated with sulphurous acid, when the iso*quinolinium iodide* separated as a mass of yellow crystals (2·7 g.). It crystallised from boiling alcohol in fine, yellow rhombs melting at 200° to a red liquid (Found : C, 51·2; H, 5·2. $C_{20}H_{24}O_4NI$ requires C, 51·2; H, 5·2%). This iodide is sparingly soluble in alcohol or water in the cold, but readily soluble on boiling.

1-*Hydroxy*-6 : 7 : 2′ : 3′-*tetramethoxy*-2-*benzyl*-1 : 2 : 3 : 4-*tetrahydro*isoquinoline (IX).—The iodide (VIII) was converted into the corresponding chloride by boiling for 1 hour with water and freshly-precipitated silver chloride, and the filtrate concentrated, cooled, and made strongly alkaline with sodium hydroxide. The white, amorphous precipitate of the *ψ-base* (IX) was collected, dissolved in dilute hydrochloric acid, reprecipitated with sodium hydroxide, thoroughly washed, and dried in a desiccator (Found : C, 66·3; H, 7·0. $C_{20}H_{25}O_5N$ requires C, 66·8; H, 7·0%).

The *ψ*-base (IX) is soluble in ether, benzene, chloroform, acetone, or alcohol, and sparingly soluble in petroleum. Attempts to obtain it in the crystalline condition were unsuccessful. The alcoholic solution exhibits a green fluorescence and the solution in concentrated sulphuric acid becomes blood-red on the addition of nitric acid. The *picrate* was prepared by adding picric acid to the alcoholic solution of the *ψ*-base and separated from alcohol in bright yellow needles, m. p. 135° (decomp.).

The *zinc chloride* derivative separated as a yellow gum when a solution of zinc chloride was added to a solution of the *ψ*-base in dilute acetic acid. The gum was dissolved in hot methyl alcohol and allowed to cool slowly, when the double salt crystallised in large, pale yellow, truncated octahedra, m. p. 158—160°.

6 : 7 : 2′ : 3′-*Tetramethoxy*-2-*benzyl*-3 : 4-*dihydro*-1-iso*quinolone* (XI).—This was prepared by boiling an alcoholic solution of the dihydro*iso*quinolinium iodide (VIII) with excess of 50% potassium hydroxide for 1 hour. The mixture was cooled and poured into water, when a red oil separated. The liquid was decanted, the oil washed with dilute hydrochloric acid and boiled with methyl alcohol, from which the substance separated in colourless prisms, m. p. 160° (Found : C, 67·2; H, 6·4. $C_{20}H_{23}O_5N$ requires C, 67·2; H, 6·4%). This *iso*quinolone is readily soluble in alcohol, ether, or benzene and almost insoluble in petroleum. It dissolves in glacial acetic acid and in concentrated mineral acids, but is reprecipitated on dilution with water.

6 : 7 : 2′ : 3′-*Tetramethoxy*-2-*benzyl*-1-*nitromethyl*-1 : 2 : 3 : 4-*tetrahydro*isoquinoline (XII).—The dihydro*iso*quinolinium iodide (VIII; 2·3 g.) was dissolved in warm methyl alcohol (15 c.c.) containing nitromethane (1 g.), a methyl-alcoholic solution of potassium

hydroxide (0·5 g.) slowly added, the mixture cooled and allowed to remain over-night, and the *nitromethyl* derivative, which had separated, washed with water. It crystallised from methyl alcohol in slender needles, m. p. 111—112° (Found: C, 62·5; H, 6·5; N, 6·9. $C_{21}H_{26}O_6N_2$ requires C, 62·7; H, 6·5; N, 7·0%).

This nitromethyl derivative is soluble in hot alcohol, benzene, or chloroform, sparingly soluble in ether, and still less soluble in petroleum. It dissolves in dilute acids and is reprecipitated on the addition of ammonia or potassium acetate. When a solution in moderately concentrated acid is heated, a salt of the ψ-base is produced. A sodium salt is formed when sodium methoxide is added to a methyl-alcoholic solution of the nitromethyl derivative, and a clear solution is obtained on diluting with water. The action of reducing agents—such as stannous chloride, zinc dust and sodium hydroxide, sodium amalgam in acid, alkaline, or neutral solution, or colloidal palladium and hydrogen—led, in all cases, to the elimination of methylamine and regeneration of the ψ-base.

6 : 7-*Methylenedioxy*-2′ : 3′-*dimethoxy*-2-*benzyl*-1-*nitromethyl*-1 : 2 : 3 : 4-*tetrahydro*isoquinoline (XV).—Norhydrohydrastinine was prepared from *N*-formylhomopiperonylamine by Decker's method (D.R.-P. 245025). Molecular proportions of this substance and 2 : 3-dimethoxybenzyl bromide were allowed to react at the ordinary temperature for 12 hours in benzene solution, when the quaternary ammonium bromide separated as a brown, crystalline mass. This was dissolved in methyl alcohol and left over-night with nitromethane (1·5 mols.) and potassium hydroxide (2 mols.); the nitromethyl derivative was then collected, washed with water, and crystallised from much alcohol, from which it separated in small needles, m. p. 135—136° (Found: C, 62·0; H, 5·7. $C_{20}H_{22}O_6N_2$ requires C, 62·1; H, 5·7%). It is explained on p. 1436 that attempts to reduce this substance to the corresponding oxime were again unsuccessful.

1-*Cyano*-6 : 7 : 2′ : 3′-*tetramethoxy*-2-*benzyl*-1 : 2 : 3 : 4-*tetrahydro*isoquinoline (X).—When a concentrated solution of potassium cyanide was added to an aqueous solution of the dihydro*iso*quinolinium iodide (VIII), the *ψ-cyanide* (X) rapidly separated as a white, crystalline precipitate, which crystallised from alcohol in brilliant, cubic crystals, m. p. 125° (Found: C, 68·4; H, 6·5; N, 7·4. $C_{21}H_{24}O_4N_2$ requires C, 68·5; H, 6·5; N, 7·6%). This ψ-cyanide is readily soluble in benzene, chloroform, or warm alcohol, sparingly soluble in ether or petroleum. The alcoholic solution exhibits a green fluorescence and the cyanide is rapidly converted into salts of the dihydro*iso*quinolinium type (VIII) by mineral acids. When an ethereal solution of iodine is added to the benzene solution of

the ψ-cyanide, a black periodide is precipitated which is converted into the dihydro*iso*quinolinium iodide (VIII) by the action of sulphurous acid.

6 : 7 : 2′ : 3′ - *Tetramethoxy* - 2 - *benzyl* - 1 - *methyl*- 1 : 2 : 3 : 4 - *tetrahydro*isoquinoline (XVIII).—A solution of the ψ-cyanide (X; 1 mol.) in anisole was added to an anisole solution of magnesium methyl iodide (3 mols.), when a yellow precipitate was produced which became grey on warming on the water-bath for an hour. The mixture was decomposed with dilute hydrochloric acid, and the hydriodide of the base, which separated as an oil, decomposed by potassium hydroxide to the corresponding base. This could not be obtained in the crystalline condition, but the *picrate*, prepared by adding picric acid to an alcoholic solution of the base, separated from alcohol in needles, m. p. 157—158° (Found: C, 55·1; H, 5·4. $C_{21}H_{27}O_4N,C_6H_3O_7N_3$ requires C, 55·3; H, 5·1%). The base was liberated from the picrate by the action of ammonia as an oil and, on oxidising the alcoholic solution of the base with iodine, oily products were obtained which did not condense with nitrosodimethylaniline (p. 1436).

1-*Cyano*-6 : 7-*dimethoxy*-2-*benzoyl*-1 : 2-*dihydro*isoquinoline (XIX).—6 : 7-Dimethoxy*iso*quinoline (22 g.) was mixed with aqueous potassium cyanide (300 c.c. of 10%) and shaken with benzoyl chloride (33 g.), when a yellow colour developed and an orange semi-solid substance was gradually deposited. The liquid was decanted, the residue washed with 10% hydrochloric acid and shaken with ether, when it solidified (yield 35%). This cyano-benzoyl derivative (XIX) separates from alcohol in colourless needles, m. p. 164° (Found: C, 71·5; H, 5·0; N, 9·1. $C_{19}H_{16}O_3N_2$ requires C, 71·2; H, 5·0; N, 8·7%).

1 - *Cyano* - 6 : 7 : 2′ : 3′ - *tetramethoxy* - 2 - *benzoyl* - 1 : 2 - *dihydro*isoquinoline.—2 : 3-*Dimethoxybenzoyl chloride* was prepared by heating the acid (20 g.) with a slight excess of thionyl chloride, the excess was removed by distillation, and the crude oil, which slowly solidified, condensed with 6 : 7-dimethoxy*iso*quinoline (11 g.) and 10% potassium cyanide solution (150 c.c.). The product (12 g.) solidified rapidly and was crystallised from glacial acetic acid, from which it separated in needles, m. p. 181° (Found: C, 65·8; H, 5·4. $C_{21}H_{20}O_5N_2$ requires C, 66·3; H, 5·3%).

6 : 7-*Dimethoxy*isoquinoline-1-*carboxylamide* (XX).—This was obtained by the action of hydrogen chloride on either of the cyano-benzoyl derivatives described above. The cyano-benzoyl derivative (XIX; 3·5 g.) was dissolved in dry chloroform, cooled in a freezing mixture, and saturated with dry hydrogen chloride, when the solution became yellow, a green fluorescence developed, and, after

some time, a mass of orange needles separated. These were washed with ether, suspended in water, and distilled in steam, when benzaldehyde was removed. The residue was filtered from traces of impurity, made alkaline with ammonia, and the precipitate (1·5 g.) collected, washed with water, and crystallised from alcohol, separating in long needles, m. p. 168—169° (Found: C, 62·1; H, 5·2; N, 11·8. $C_{12}H_{12}O_3N_2$ requires C, 62·1; H, 5·2; N, 12·0%). This amide (XX) is readily soluble in hot water and, on the addition of mercuric chloride, a double compound separates which crystallises from hot water in long, colourless needles. The amide cannot be hydrolysed to the corresponding acid either by acids or alkalis, but a small amount of the acid was obtained from the ammoniacal mother-liquors of the above preparation, by rendering faintly acid with acetic acid and adding copper acetate, when a pale green copper salt separated. On decomposition with hydrogen sulphate, this yielded a small quantity of 6 : 7-dimethoxy*iso*quinoline-1-carboxylic acid identical with the acid obtained by Goldschmiedt (*Monatsh.*, 1885, **6**, 964; 1887, **8**, 520) by the oxidation of papaverine. The mercuric chloride derivative of this acid is sparingly soluble in water, from which it separates in small needles.

6 : 7 : 2′ : 3′ - *Tetramethoxy* - 2 - *benzyl* - 1 : 2 : 3 : 4 - *tetrahydro*iso - *quinoline*-1-*carboxylamide* (XVII).—The ψ-cyanide (X; 1·5 g.) was dissolved in freshly distilled anisole (30 c.c.), containing fused zinc chloride (2 g.) in suspension, and the solution saturated with dry hydrogen chloride, the temperature being maintained below 15°. A brown gum separated on the zinc chloride and, after 3 hours, most of the solvent was decanted, the gum dissolved in hot water, and the last traces of anisole were removed in a current of steam. The residue was mixed with a solution of ammonia and ammonium chloride, the pale yellow solid collected and crystallised from benzene, from which the amide separated in colourless needles, m. p. 192°.

The yield varied in different experiments from nothing to about 25% of the theoretical, and the exact conditions for successful preparation could not be determined. In all the experiments much of the ψ-cyanide (X) was converted into the dihydro*iso*quinolinium chloride of type (VIII). A more trustworthy method for the preparation of the amide (XVII) is the following: Equimolecular proportions of 2 : 3-dimethoxybenzyl bromide and 6 : 7-dimethoxy-*iso*quinoline-1-carboxylamide (XX) are boiled for 24 hours in toluene solution, when the ammonium bromide separates as a brown, crystalline powder which does not melt at 250° (Found: Br, 17·0. $C_{21}H_{23}O_5N_2Br$ requires Br, 17·2%).

This bromide is reduced by boiling in much alcohol with a large excess of granulated tin and hydrochloric acid for 12 hours, the

alcohol is removed by distillation and the residue poured into water, when a sticky tin double salt separates. This is suspended in boiling water and decomposed by hydrogen sulphide. The filtrate, made alkaline by ammonia, deposits the amide (XVII), which is then recrystallised from benzene (Found: C, 64·9; H, 6·7; N, 7·3. $C_{21}H_{26}O_5N_2$ requires C, 65·3; H, 6·7; N, 7·3%).

This amide dissolves readily in dilute acids, but, even after boiling with concentrated hydrochloric acid or alcoholic potassium hydroxide, it can be recovered unchanged.

Anhydrocotarnine-methylamine (XVI).—Anhydrocotarnine-nitromethane (5 g.) was dissolved in methyl alcohol containing sodium methoxide (Na = 1 g.) and poured into a 30% solution of sodium hydroxide (50 c.c.). The clear solution was heated at 60° and zinc dust (40 g.) added in small portions during 2 hours. The mixture was extracted with ether, the extract dried over potassium carbonate and the solvent removed, when a pale yellow oil remained which decomposed on distillation. The *dihydrochloride*, precipitated on saturating the ethereal solution of the base with dry hydrogen chloride, is readily soluble in water and alcohol and can be crystallised from alcohol–ether in long needles, m. p. 227° (Found: N, 8·6; Cl, 21·4. $C_{13}H_{20}O_3N_2Cl_2$ requires N, 8·7; Cl, 21·9%).

The *picrate*, prepared by adding picric acid to the alcoholic solution of the base, is sparingly soluble and melts at 200° (decomp.). Anhydrocotarnine-methylamine may also be obtained by reducing anhydrocotarnine-nitromethane with stannous chloride and hydrochloric acid in the cold.

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OXFORD.

[*Received, April 28th*, 1925.]

CXCV.—*Synthetical Experiments in the* iso*Quinoline Group. Part II.*

By ROBERT DOWNS HAWORTH, WILLIAM HENRY PERKIN, jun., and JOHN RANKIN.

IN Part I of this series (preceding paper) an account has been given of an unsuccessful attempt to achieve a synthesis of alkaloids of the berberine group from 6 : 7 : 2′ : 3′-tetramethoxy-2-benzyl-1 : 2 : 3 : 4-tetrahydro*iso*quinoline and its derivatives. The earlier stages of this investigation were rendered difficult because of the limited supply of *o*-vanillin at our disposal, and it was therefore thought advisable that a series of experiments similar to those described in Part I should first be carried out with the more accessible ordinary vanillin. The present communication contains

an account of the preparation and properties of the substances studied during this investigation.

3 : 4-*Dimethoxybenzyl Bromide.*—3 : 4-Dimethoxybenzyl alcohol, prepared by the action of alcoholic potassium hydroxide on 3 : 4-dimethoxybenzaldehyde (Tiffeneau, *Bull. Soc. chim.*, 1911, 9, 929), dissolved in eight times its weight of dry benzene, was saturated with dry hydrogen bromide at 10°, the product neutralised by calcium carbonate, filtered, and the benzene removed by distillation under reduced pressure. The colourless oil remaining could not be distilled under reduced pressure owing to decomposition with loss of hydrogen bromide and formation of a green substance, but, after remaining in an evacuated desiccator for several days, it slowly solidified (Found : Br, 33·9. $C_9H_{11}O_2Br$ requires Br, 34·6%).

This bromide is very soluble in the usual organic solvents and is rapidly hydrolysed by moisture. It has very slight lachrymatory properties and this fact is somewhat remarkable in view of the pungent character of 2 : 3-dimethoxybenzyl bromide (p. 1437).

6 : 7 : 3′ : 4′-*Tetramethoxy*-2-*benzyl*iso*quinolinium Bromide* (compare III).*—Equimolecular proportions of crude 3 : 4-dimethoxybenzyl bromide and 6 : 7-dimethoxy*iso*quinoline were allowed to react in benzene solution. After remaining over-night, the separation of the bromide was practically complete and the pale yellow precipitate was collected and washed with benzene. The nearly pure bromide, obtained in excellent yield, separated from water in clusters of slender needles, m. p. 137—138° (Found : C, 57·1; H, 5·5; Br, 18·7. $C_{20}H_{22}O_4NBr$ requires C, 57·1; H, 5·2; Br, 19·0%). The corresponding *iodide* was obtained by the addition of potassium iodide to the warm aqueous solution of the bromide, when a precipitate formed immediately and increased on cooling the solution. It was almost insoluble in cold and only slightly soluble in boiling water, but dissolved readily in boiling methyl alcohol and separated in long, thin, pale yellow prisms, m. p. 203—204° (Found : I, 27·1. $C_{20}H_{22}O_4NI$ requires I, 27·2%).

1-*Hydroxy*-6 : 7 : 3′ : 4′-*tetramethoxy*-2-*benzyl*-1 : 2-*dihydro*iso-*quinoline* (compare IV).—This was prepared by the addition of excess of sodium hydroxide to the cold aqueous solution of the bromide (compare III), when no immediate precipitation took place, but after some time the ψ-base separated as a colourless, flocculent precipitate. This ψ-base (compare IV) could not be recrystallised and rapidly darkened and shrank to a plastic mass

* The formulæ of the substances described in this communication differ from those described in Part I only in the position of two methoxy-groups, and the numbers inserted here refer to the formulæ of the corresponding substances in Part I.

on exposure to air. The base, rapidly dried in an evacuated desiccator, was analysed (Found: C, 67·1; H, 6·2; N, 3·9. $C_{20}H_{23}O_5N$ requires C, 67·2; H, 6·4; N, 3·9%).

6 : 7 : 3′ : 4′-*Tetramethoxy*-2-*benzyl*-1-iso*quinoline* (compare VI).—An alcoholic solution of the bromide (compare III) was heated with a large excess of alcoholic potassium hydroxide, most of the alcohol removed by distillation, and the residue diluted with water, when an oil separated. This was washed by decantation, dissolved in a large excess of boiling hydrochloric acid (20%), and a few drops of alcohol were added; on cooling, colourless, slender needles separated, m. p. 128—129° (Found: C, 67·4; H, 5·9. $C_{20}H_{21}O_5N$ requires C, 67·6; H, 5·9%).

1-*Cyano*-6 : 7 : 3′ : 4′-*tetramethoxy*-2-*benzyl*-1 : 2-*dihydro*isoquinoline (compare V).—When a solution of potassium cyanide was added to an aqueous solution of the bromide (compare III) the *ψ-cyanide* was precipitated as an oil which solidified on stirring. It was collected, washed well, and dried in a desiccator (Found: N, 7·8. $C_{21}H_{22}O_4N_2$ requires N, 7·6%).

This ψ-cyanide is readily soluble in the usual organic solvents and rapidly loses hydrogen cyanide on treatment with dilute acids. It is moderately soluble in water, from which it is reprecipitated by potassium cyanide. A small quantity of the ψ-cyanide was obtained in the crystalline state by allowing its aqueous solution to drop slowly into a very dilute solution of potassium cyanide. After standing for about 10 days, the ψ-cyanide had separated in colourless needles which darkened at 115° and melted at 117° (decomp.).

6 : 7 : 3′ : 4′-*Tetramethoxy*-2-*benzyl*-1 : 2 : 3 : 4-*tetrahydro*isoquinoline (compare I).—The bromide (compare III; 5 g.) was dissolved in a mixture of alcohol (150 c.c.) and concentrated hydrochloric acid (150 c.c.), boiled over-night with an excess of granulated tin, the alcohol removed by distillation, and the residue decanted from the tin into water. The liquid, with the tin double salt in fine suspension, was heated to boiling, when the double salt coagulated in a form which allowed of filtration. It was suspended in boiling water, decomposed with hydrogen sulphide, the filtrate concentrated and made alkaline with sodium hydroxide, when the *tetrahydro*iso*quinoline* was precipitated as a grey, slightly viscous solid. This (2·4 g.) crystallised from ether in colourless prisms, m. p. 93° (Found: C, 69·7; H, 7·3. $C_{20}H_{25}O_4N$ requires C, 70·0; H, 7·3%). The base is readily soluble in dilute acids and does not react with methylal, acetal, or sulphoacetic acid (compare p. 1434).

6 : 7 : 3′ : 4′-*Tetramethoxy*-2-*benzyl*-3 : 4-*dihydro*isoquinolinium *Iodide* (compare VIII).—The base (compare I; 5 g.) was dissolved in alcohol (30 c.c.), containing potassium acetate (2 g.), and heated

on the steam-bath during the addition of an alcoholic solution of iodine (40 c.c. of 10%). Most of the alcohol was removed by distillation and the dark brown residue treated with sulphurous acid, when small, orange crystals separated which, after crystallisation, melted at 184—185° (Found : C, 51·5; H, 5·3. $C_{20}H_{24}O_4NI$ requires C, 51·2; H, 5·1%). This iodide dissolves in boiling alcohol, but is sparingly soluble in hot and almost insoluble in cold water. A *periodide* was obtained as a dark brown precipitate on the addition of an alcoholic solution of iodine to an alcoholic solution of the iodide and crystallised from anisole in small, brown needles, m. p. 160° (Found : C, 33·7; H, 3·5; I, 52·4. $C_{20}H_{24}O_4NI_3$ requires C, 33·2; H, 3·3; I, 52·7%). The *chloride*, prepared from the iodide by treatment with silver chloride, separated from a little water in large, yellow rhombs melting indefinitely at 52—56° and containing solvent of crystallisation. The loss of weight on drying at 120° was 15·5% and the dry substance gave C, 63·2; H, 6·5. $C_{20}H_{24}O_4NCl$ requires C, 63·3; H, 6·3%.

1-*Hydroxy*-6 : 7 : 3′ : 4′-*tetramethoxy*-2-*benzyl*-1 : 2 : 3 : 4-*tetrahydro*iso*quinoline* (compare IX).—This substance separated as an amorphous precipitate when sodium hydroxide was added to the solution of the above chloride. It could not be obtained crystalline and darkened on exposure to air. The corresponding iso*quinolone* (compare XI) may be obtained by warming an alcoholic solution of the above iodide with alcoholic potassium hydroxide, but is more conveniently prepared in the following way. The iodide (3 g.) and potassium hydroxide (0·75 g.) are dissolved in alcohol and treated with a solution of potassium ferricyanide (4·25 g.) in the minimum of water. After heating on the steam-bath for 2 hours, most of the alcohol is removed by distillation, and the solution extracted several times with ether. The ethereal extract is well washed with dilute hydrochloric acid, and the ether allowed to evaporate slowly, when the *iso*quinolone separates in large, amber, rhombic crystals, m. p. 116° (Found : C, 67·3; H, 6·2. $C_{20}H_{23}O_5N$ requires C, 67·2; H, 6·4%).

1-*Cyano*-6 : 7 : 3′ : 4′-*tetramethoxy*-2-*benzyl*-1 : 2 : 3 : 4-*tetrahydro*iso*quinoline* (compare X).—This was prepared by the addition of a concentrated solution of potassium cyanide to an aqueous solution of the chloride described above. The *ψ-cyanide* was collected, dissolved in ether, dried over potassium carbonate, and the ether allowed to evaporate slowly, when colourless, cubic crystals separated, m. p. 98° (Found : C, 68·3; H, 6·6; N, 7·4. $C_{21}H_{24}O_4N_2$ requires C, 68·5; H, 6·5; N, 7·6%). This ψ-cyanide is readily soluble in alcohol, and the solution exhibits a green fluorescence.

6 : 7 : 3′ : 4′-*Tetramethoxy*-2-*benzyl*-1-*nitromethyl*-1 : 2 : 3 : 4-*tetrahydro*iso*quinoline* (compare XII).—The iodide (see above) (2·3 g.),

nitromethane (1 g.), and potassium hydroxide (0·5 g.) were allowed to react over-night in methyl-alcoholic solution (20 c.c.). The *nitromethyl* derivative, after being washed with water, separated from methyl alcohol in colourless needles, m. p. 148—149° (Found: C, 62·6; H, 6·5; N, 6·7. $C_{21}H_{26}O_6N_2$ requires C, 62·7; H, 6·5; N, 6·9%). In its behaviour with reducing agents, this nitromethyl derivative resembles the isomeric substance described in Part I (p. 1441), methylamine and a derivative of the ψ-base being produced.

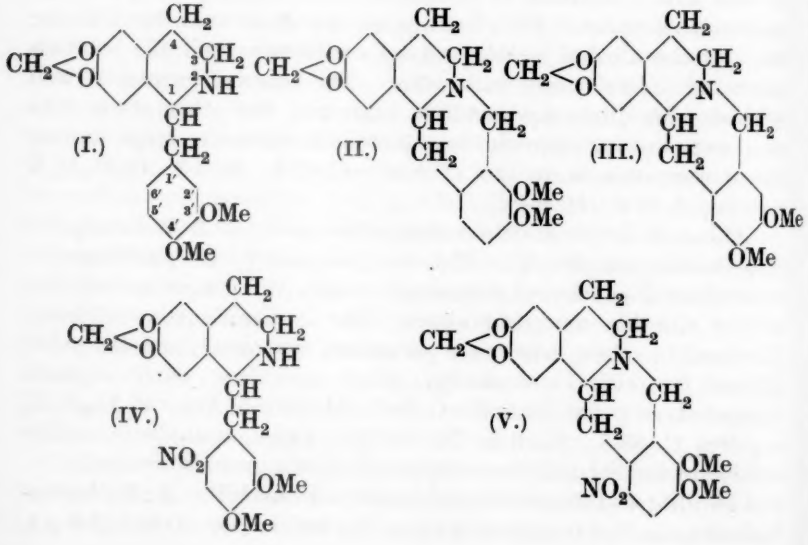
THE DYSON PERRINS LABORATORY,
OXFORD.

[*Received, April 28th,* 1925.]

CXCVI.—*Synthetical Experiments in the* iso*Quinoline Group. Part III.*

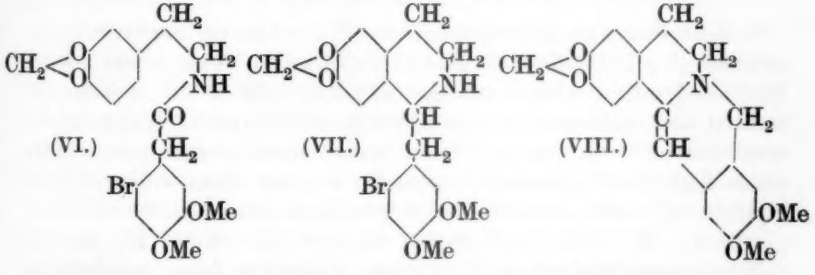
By ROBERT DOWNS HAWORTH and WILLIAM HENRY PERKIN, jun.

IT has been shown by Haworth, Perkin, and Rankin (J., 1924, **125**, 1685) that veratrylnorhydrohydrastinine (I), on treatment with formaldehyde and hydrochloric acid, yields a substance isomeric with tetrahydroberberine (II) and to this substance (III) the name tetrahydro-ψ-berberine was given. The present communication contains an account of some experiments which have been instituted with the object of determining whether it is possible to convert veratrylnorhydrohydrastinine into tetrahydroberberine by indirect methods.



When veratrylnorhydrohydrastinine reacted, in glacial acetic acid solution, with nitric acid which had previously been treated with carbamide, a mononitro-derivative was obtained. This proved to be 6-*nitroveratrylnorhydrohydrastinine* (IV), because, on reduction with zinc dust and hydrochloric acid, an amino-derivative was obtained which gave the greenish-blue coloration with ferric chloride characteristic of *p*-anisidines.

It is clear from the consideration of the formula that this 6-nitro-derivative might conceivably yield 6-nitrotetrahydroberberine (V) on treatment with formaldehyde and hydrochloric acid. When the experiment was tried, it was found that, although the substance (IV) interacts readily with formaldehyde, the product yields no trace of nitrotetrahydroberberine on treatment with hydrochloric acid. As this failure may have been due to the well-known inhibiting effect of the nitro-group, we next carried out a similar series of experiments with the corresponding derivative of veratrylnorhydrohydrastinine containing a bromine atom in the place of the nitro-group. 6-Bromoveratrylnorhydrohydrastinine could not be obtained pure by the direct action of bromine and in order to synthesise it, 6-bromohomoveratric acid was prepared by the bromination of homoveratric acid and found to be identical with the acid which Pschorr (*Annalen*, 1912, **391**, 35) had already obtained by another process. When equimolecular proportions of homopiperonylamine and 6-bromohomoveratric acid were heated at 180°, excellent yields of 6-bromohomoveratroylhomopiperonylamine (VI) were obtained. This was treated with phosphorus oxychloride in toluene solution, and the product directly reduced with zinc and dilute sulphuric acid, when 6-*bromoveratrylnorhydrohydrastinine* (VII) was readily obtained pure and in good yield. This bromo-derivative reacted readily with formaldehyde, but bromoveratrylnorhydrohydrastinine was recovered when the condensation product was treated with hydrochloric acid and no trace of bromotetrahydroberberine (V, with Br for NO_2) could be isolated.



We next prepared 2-formylbromoveratrylnorhydrohydrastinine by heating 6-bromoveratrylnorhydrohydrastinine (VII) with one

molecular proportion of formic acid at 180° and found that this formyl derivative, when treated in the usual manner with phosphorus oxychloride in toluene solution followed by reduction with zinc dust and sulphuric acid, yielded tetrahydro-ψ-berberine (III, *loc. cit.*, p. 1688). This remarkable result shows that, rather than close the *iso*quinoline ring with the aid of the >CH group in the 2′-position of the veratryl nucleus (compare I), the tendency to ring closure in the 6′-position is so great that it will proceed in this direction even when this closure necessitates the elimination of the bromine atom occupying that position.

During the course of this investigation we examined the action of phosphorus oxychloride on the 2′-formyl derivative of veratrylnorhydrohydrastinine (I) and obtained an excellent yield of dihydro-ψ-berberine (VIII) identical with the basic product obtained by the action of sodium hydroxide on ψ-berberinium chloride (*loc. cit.*, p. 1691). In connexion with this and other investigations in the same group, it became very desirable to have some method for rapidly distinguishing between bases of the berberine and ψ-berberine types, and we are indebted to Professor Robinson for the following device which has been found to yield excellent results. Examination of the respective formulæ shows that the structure of tetrahydroberberine (II) differs from that of tetrahydro-ψ-berberine (III) in containing a free position para to a methoxy-group. It was therefore to be expected that tetrahydroberberine would nitrate much more readily than the isomeric base and this has proved to be the case. When tetrahydroberberine is treated with nitric acid in glacial acetic acid solution, 6-*nitrotetrahydroberberine* (V) is obtained and this, on reduction with zinc dust and hydrochloric acid in alcoholic solution, yields an amino-derivative which gives a blue coloration with ferric chloride. Under the same conditions, tetrahydro-ψ-berberine undergoes oxidation and does not yield a nitro-derivative.

EXPERIMENTAL.

6′-*Nitroveratrylnorhydrohydrastinine* (IV).—Veratrylnorhydrohydrastinine (5 g.), dissolved in glacial acetic acid (15 c.c.), was cooled to 0° and mixed with a solution of nitric acid (5 c.c., previously treated with carbamide) in glacial acetic acid (15 c.c.). The mixture was allowed to remain at 0° for a few minutes, poured into water, made slightly alkaline with ammonia, and the cream-coloured precipitate collected, washed, and crystallised from alcohol (Found: C, 64·5; H, 5·3. $C_{19}H_{20}O_6N_2$ requires C, 64·5; H, 5·4%). 6-Nitroveratrylnorhydrohydrastinine separates from alcohol in pale yellow prisms, melts at 149—150°, and slowly becomes green

on exposure to air. This nitro-derivative, dissolved in alcohol containing a little hydrochloric acid and treated with excess of zinc dust, is rapidly reduced; the solution, after filtering, gives a greenish-blue coloration on the addition of a drop of ferric chloride. When the nitro-derivative, dissolved in methyl alcohol, is warmed for a few minutes with formalin, the additive compound is produced and is precipitated as a gum on diluting with water. This was dissolved in concentrated hydrochloric acid and heated under varying conditions on the steam-bath, but in no case could the formation of any nitrotetrahydroberberine be detected.

6-*Nitrotetrahydroberberine* (V).—This substance is readily produced when tetrahydroberberine, dissolved in glacial acetic acid, is mixed with nitric acid; on pouring into water and rendering alkaline with ammonia, the base is precipitated and may be recrystallised from alcohol (Found: N, 7·3. $C_{20}H_{20}O_6N_2$ requires N, 7·3%). This nitro-derivative separates from alcohol or benzene in small, buff-coloured needles, m. p. 185°. It is readily soluble in dilute hydrochloric acid; the amino-derivative produced on the addition of zinc dust gives a greenish-blue coloration with ferric chloride.

6′-*Bromohomoveratroylhomopiperonylamine* (VI).—6-Bromohomoveratric acid was prepared by adding bromine (9 g.) to a solution of homoveratric acid (10 g.) in glacial acetic acid (50 c.c.). After remaining over-night, the crude bromohomoveratric acid was collected; it had the properties described by Pschorr (*loc. cit.*). After gradual crystallisation from water, it sintered at 80°, but rapid crystallisation yielded the acid of m. p. 115°.

The substance (VI) was prepared by heating molecular proportions of the bromohomoveratric acid and homopiperonylamine for one and a half hours at 180°; it crystallised from alcohol in large, rectangular plates, m. p. 159—160° (Found: C, 54·1; H, 4·8. $C_{19}H_{19}O_5NBr$ requires C, 54·1; H, 4·5%). When this substance (5 g.), dissolved in toluene (30 c.c.), was heated with phosphorus oxychloride (12 c.c.) for 1¼ hours, condensation took place readily. The whole was diluted with petroleum (b. p. 40—60°), the solvent decanted from the syrup, the latter dissolved in alcohol, made alkaline with sodium hydroxide, and extracted with benzene. The crude 6′-bromoveratryldihydro*iso*quinoline was extracted from the benzene solution by dilute sulphuric acid and heated on the water-bath for ½ hour with an excess of zinc dust.* The hot solution was filtered, made alkaline with ammonia, extracted with chloroform, the extract dried over potassium carbonate, the solvent removed by distillation, and the residue crystallised from methyl

* When reduction was allowed to proceed for more than ½ hour, considerable quantities of veratrylnorhydrohydrastinine were formed.

alcohol (Found: C, 56·4; H, 5·0. $C_{19}H_{20}O_4NBr$ requires C, 56·2; H, 4·9%). 6′-*Bromoveratrylnorhydrohydrastinine* separates from methyl alcohol in long, colourless needles, m. p. 159—160°. The *hydrochloride* is sparingly soluble in water, from which it crystallises in colourless needles which soften at 250° and melt at 260—262° to a red liquid. The *picrate* was prepared in alcoholic solution and crystallised from alcohol in orange needles, m. p. 174—175°. The 2-hydroxymethyl derivative was obtained by warming the methyl-alcoholic solution of the base with formalin for ½ hour on the water-bath. On diluting the solution with water, an oil separated which rapidly solidified but could not be recrystallised. The *picrate* was readily prepared in methyl-alcoholic solution and separated from methyl alcohol in yellow needles, m. p. 154—155°. The 2-hydroxymethyl derivative, dissolved in concentrated hydrochloric acid, was heated on the steam-bath for varying periods. In some cases it was recovered unchanged and identified by means of the picrate, whilst in other experiments 6′-bromoveratrylnorhydrohydrastinine was obtained.

2-*Formyl*-6′-*bromoveratrylnorhydrohydrastinine*.—A benzene solution of 6′-bromoveratrylnorhydrohydrastinine was mixed with the calculated amount of anhydrous formic acid, when the formate separated as a white, crystalline mass. The benzene was then removed by distillation and the formate heated at 180° for 3 hours. The formyl derivative solidified, on cooling, to a crystalline mass (5 g.), and without further purification was dissolved in toluene (30 c.c.) and heated with phosphorus oxychloride (12 c.c.), when a red oil separated. After ½ hour, excess of petroleum (b. p. 40—60°) was added, the solvent decanted, the residual syrup dissolved in alcohol, mixed with dilute sulphuric acid and reduced with zinc dust during 4 hours. After filtration, the colourless solution was made alkaline with ammonia, extracted with chloroform, dried over potassium carbonate, the chloroform removed by distillation, and the residue crystallised from alcohol. The substance separated in long, colourless needles, melted at 177°, contained no bromine, and was shown to be tetrahydro-ψ-berberine (III) by the mixed melting point method. Identity was confirmed by the preparation of the hydrochloride (m. p. 220°) and the picrate (m. p. 176°).

Action of Phosphorus Oxychloride on 2-*Formylveratrylnorhydrohydrastinine*.—Veratrylnorhydrohydrastinine (5 g.) was dissolved in benzene (20 c.c.) and treated with the calculated amount of anhydrous formic acid, when the white crystalline formate separated. The benzene was removed by distillation and the residue heated at 180° for 3 hours, when the decomposition was complete. The crude formyl derivative was dissolved in toluene (30 c.c.) and

heated in the usual manner with phosphorus oxychloride for 1½ hours. The mixture was cooled, shaken with petroleum, the solvent decanted, and the residual syrup dissolved in alcohol, made alkaline with ammonia, diluted with water, and the pale yellow precipitate collected. It crystallised from alcohol or acetone in pale yellow needles, melted sharply at 154—155°,* and proved to be identical with a specimen of dihydroanhydro-ψ-berberine which had been obtained by the action of sodium hydroxide on ψ-berberinium chloride (J., 1924, **125**, 1699). This was confirmed by a mixed melting point and by the preparation of the hydrochloride (m. p. 253—255°, decomp.).

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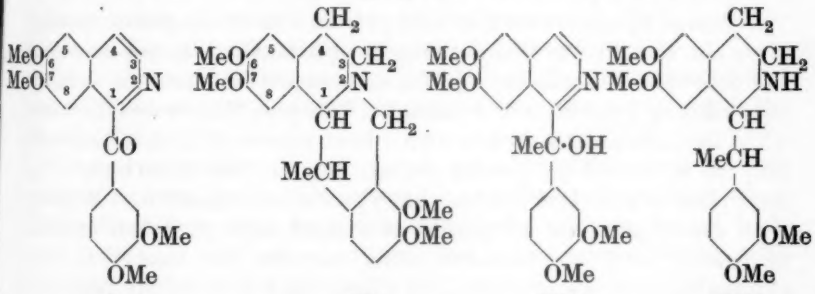
[*Received, April 28th*, 1925.]

CXCVII.—*Synthetical Experiments in the* iso*Quinoline Group. Part IV.*

By ROBERT DOWNS HAWORTH and WILLIAM HENRY PERKIN, jun.

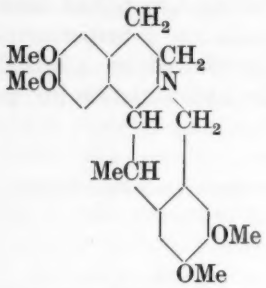
IN the preceding sections of this investigation experiments were described which had for their object the synthesis of certain of the berberine alkaloids, *e.g.*, berberine, palmatine, and corydaline. The present communication deals mainly with an attempt to convert papaveraldine (I) into corydaline (II). The constitution of papaveraldine was first determined analytically by Goldschmiedt (*Monatsh.*, 1886, **7**, 185; 1888, **9**, 8) and the substance has recently been synthesised by Buck, Haworth, and Perkin (J., 1924, **125**, 2176).



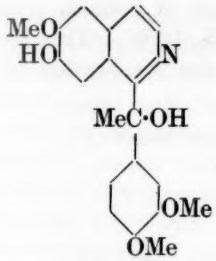
(I.) (II.) (III.) (IV.)

* We should like to take this opportunity of correcting two melting points recorded in our previous communication (J., 1924, **125**, 1686). The melting point of dihydro-ψ-berberine is 154—155° and not 165—167° (p. 1699) and the melting point of *N*-*o*-nitrobenzoylnorhydrohydrastinine is 160—161° and not 154° (p. 1700).

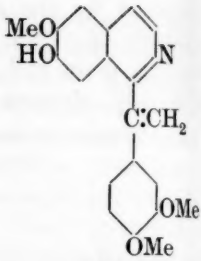
It seemed reasonable to suppose that papaveraldine, on treatment with magnesium methyl iodide, might yield methylpapaveraldine (III) and that this on reduction would be converted into methyltetrahydropapaverine (IV). Finally, this substance (IV), if it reacted normally with methylal or formaldehyde, should furnish either corydaline (II) or ψ-corydaline (V).



(V.)



(VI.)



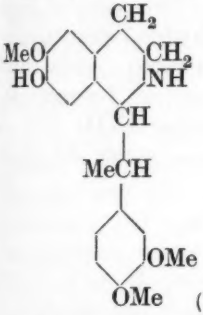
(VII.)

When an anisole solution of papaveraldine was allowed to react with one molecular proportion of magnesium methyl iodide, an orange addition product separated which regenerated papaveraldine on decomposition with hydrochloric acid, but when two molecular proportions of magnesium methyl iodide were employed a grey precipitate separated which on decomposition with acids yielded salts of a new base, $C_{20}H_{21}O_5N$ (m. p. 114—116°). During this simple decomposition, there is therefore loss of a methyl group, and as the base is also devoid of ketonic properties, there can be little doubt that it is 7-*demethylomethylpapaverinol* and that its constitution is represented by formula (VI).

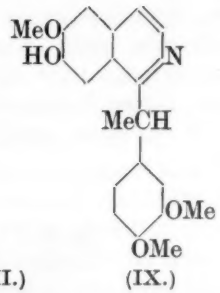
Although the elimination of methyl from a methoxy-group usually gives rise to a free hydroxyl group, it apparently does not do so in the case under discussion, for the substance (VI) does not exhibit the ordinary properties of a phenol. It is true that traces dissolve when the substance is shaken with a large excess of dilute alkali and may be recovered on passing carbon dioxide, but all attempts to methylate or acetylate the base have proved unsuccessful. Boiling with excess of acetic anhydride, treatment with phenylcarbimide, or heating with concentrated acids converts the base (VI), by elimination of 1 mol. of water, into a base which is obviously *anhydro*-7-*demethylomethylpapaverinol* (VII). This substance again behaves as though it does not contain a phenolic hydroxyl group, since it is insoluble in alkalis and cannot be methylated or acetylated.* When

* This curious behaviour has been noticed in a few other cases (compare methylnoroxyberberine: Faltis, *Monatsh.*, 1910, **31**, 557; Bland, Perkin, and Robinson, J., 1912, **101**, 262; this vol., p. 744), but the reason why these

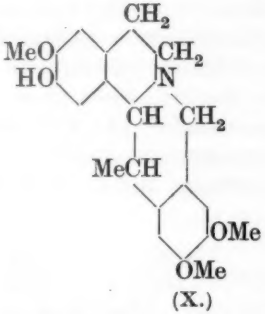
7-demethylomethylpapaverinol (VI) or the anhydro-derivative (VII) is reduced with tin and hydrochloric acid, a mixture of substances is obtained from which a base, $C_{20}H_{21}O_4N$ (m. p. 148°), has been isolated and this is probably *7-demethylomethylpapaverine* (IX). When this substance is reduced with tin and hydrochloric acid, or when the substances (VI) and (VII) are heated with a large excess of the same reducing agent, a base, $C_{20}H_{25}O_4N$ (m. p. 64—65°), is produced which contains three methoxy-groups, yields a *nitrosoamine* (m. p. 124°), and is evidently *7-demethylomethyltetrahydropapaverine* (VIII). This substance is sufficiently basic to combine with carbonic acid from the air, but again does not exhibit phenolic properties.



(VIII.)



(IX.)



(X.)

When 7-demethylomethyltetrahydropapaverine (VIII) is warmed with methylal and hydrochloric acid, an interesting new base, $C_{21}H_{25}O_4N$ (m. p. 150—151°), is produced which contains three methoxy-groups and presumably a free hydroxyl group, but attempts to methylate or acetylate the substance were again unsuccessful. The base yields well-characterised salts and the methiodide and methochloride also crystallise well.

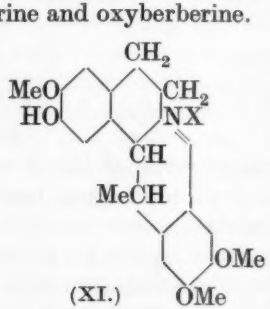
We have named this base, which has all the characteristics of tetrahydroberberine, *7-demethylo-ψ-corydaline* and assign to it the formula (X).

That this substance is related to ψ-corydaline and not to corydaline was proved by making use of the method described in Part III of this series for distinguishing between 3 : 4- and 4 : 5-disubstitution derivatives of veratrole. The base, treated with

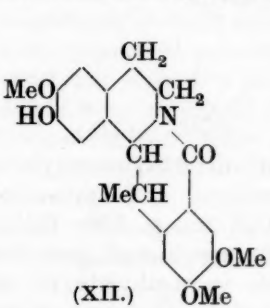
substances, produced by demethylation, do not exhibit ordinary phenolic properties is not apparent. It is possible that the grouping MeO·Ċ–Ċ(OH)– may become converted by tautomeric change into MeO·ĊH–CO–, and that, in certain positions, this may not be reconvertible into the hydroxy-modification, or the attraction between the phenolic OH-group and the basic nitrogen atom may be so powerful as to render the former inactive.

Experiments with the view of testing these and other possibilities are in progress.

nitric acid in acetic acid solution, clearly did not nitrate, and, on reduction with zinc dust and hydrochloric acid, the colourless solution did not yield the blue coloration with ferric chloride which it should have done had the original base been a derivative of corydaline. The action of the nitric acid was to produce a red substance which was clearly the result of oxidation and had properties resembling those of a substance of the berberinium type. 7-Demethylo-ψ-corydaline (X) is readily oxidised by iodine or mercuric acetate to bright yellow, crystalline salts (p. 1460) which in appearance and properties closely resemble dehydrocorydaline or berberinium salts, but analysis shows that these salts are in reality of the dihydro-7-demethylo-ψ-dehydrocorydaline type (XI. Compare Dobbie and Lauder, J., 1902, **81**, 148). This view of their constitution is confirmed by the behaviour of dihydro-7-demethylo-ψ-dehydrocorydalinium chloride with concentrated potassium hydroxide, when it is converted into a mixture of *7-demethylo-ψ-corydaline* (X) and *ketonor-7-demethylo-ψ-corydaline* (XII) just as berberinium chloride, under the same conditions, yields dihydroberberine and oxyberberine.

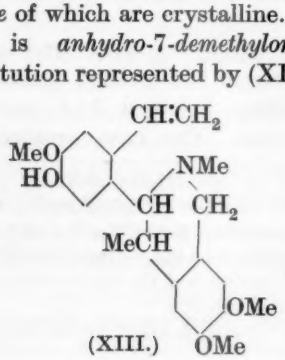


(XI.)

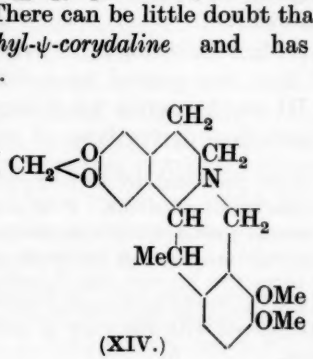


(XII.)

The *methochloride* of 7-demethylo-ψ-corydaline exhibits an interesting behaviour on boiling with potassium hydroxide, when it is converted into an oily base, $C_{22}H_{27}O_4N$, the *hydrochloride* and *picrate* of which are crystalline. There can be little doubt that this base is *anhydro-7-demethylomethyl-ψ-corydaline* and has the constitution represented by (XIII).



(XIII.)



(XIV.)

During the course of this investigation we have attempted to synthesise corydaline from the two isomeric modifications of 4-methyltetrahydroberberine (XIV. Freund and Fleischer, *Annalen*, 1915, **409**, 230) by removing the methylenedioxy-group with alcoholic potassium hydroxide (Späth and Lang, *Ber.*, 1921, **54**, 3064) and then methylating the product, but the experiments, which need not be described in detail, were not successful.

Experimental.

The Action of Magnesium Methyl Iodide on Papaveraldine.—(i) An ethereal solution of magnesium methyl iodide prepared from ether (50 c.c.), magnesium (2 g.), and methyl iodide (4·2 g.) was slowly added to a suspension of papaveraldine (10 g.) in anisole (200 c.c.), when an orange precipitate separated. After heating on the steam-bath for an hour, the mixture was decomposed with dilute hydrochloric acid, the ether–anisole layer removed, and the acid extract made alkaline with ammonia. The precipitate was boiled with methyl alcohol, in which papaveraldine is sparingly soluble, and 9 g. of the unchanged base were recovered. (ii) Papaveraldine (30 g.), suspended in anisole (500 c.c.), was mixed with magnesium methyl iodide from magnesium (6 g.), the mixture heated on the steam-bath for an hour, and the grey precipitate collected and decomposed by dilute hydrochloric acid. The acid layer was made alkaline with ammonia, when an oil separated which gradually solidified. A small second crop was obtained by saturating the ammoniacal filtrate with carbon dioxide.

7-*Demethylomethylpapaverinol* (VI) is somewhat difficult to obtain in a pure condition, but when a small portion of the crude material, dissolved in ether and mixed with petrol (b. p. 40—60°), was left in an open vessel, warts of needles melting at 112—114° gradually separated. On redissolving these in ether and precipitating with petroleum, colourless needles were obtained, m. p. 114—116° [Found: C, 67·3; H, 5·8; MeO, 27·2. $C_{20}H_{21}O_5N$ (containing 3MeO) requires C, 67·6; H, 5·9; MeO, 26·2%]. 7-Demethylomethylpapaverinol dissolves readily in dilute acids to pale yellow solutions, but concentrated acids cause dehydration and formation of the anhydro-derivative (see below). When the substance was warmed with phenylcarbimide for a few minutes, cooled, and mixed with benzene, carbanilide separated and the addition of light petroleum to the filtrate from this caused the separation of colourless needles, m. p. 151°, which were recognised as the anhydro-derivative. Attempts to acetylate 7-demethylomethylpapaverinol by boiling with acetic anhydride and potassium acetate or a few drops of sulphuric acid or camphorsulphonic acid were unsuccessful, the

product in each experiment was the anhydro-derivative. It was also not found possible to methylate the substance by repeated treatment with methyl sulphate and sodium hydroxide; in all such experiments the only substance which could be isolated was the anhydro-derivative.

Anhydro-7-demethylomethylpapaverinol (VII).—This base is readily obtained from 7-demethylomethylpapaverinol by warming for a short time with sulphuric acid (50%) and adding excess of ammonia. It was usually prepared by dissolving the crude product from the Grignard reaction (p. 1457) in concentrated hydrochloric acid, warming on the steam-bath for a short time, and leaving over-night. The hydrochloride of anhydro-7-demethylomethylpapaverinol, which had separated in pale yellow needles, was dissolved in a little water, the base liberated with ammonia, and crystallised from methyl alcohol, from which it separated in small needles, m. p. 151° (Found: C, 71·1; H, 5·7; N, 3·9. $C_{20}H_{19}O_4N$ requires C, 71·2; H, 5·6; N, 4·1%). This anhydro-derivative is readily soluble in dilute acids to pale yellow solutions; the picrate separates from methyl alcohol in groups of small needles, m. p. 110—112° (decomp.); the *perchlorate* crystallises from aqueous methyl alcohol in pale yellow plates, m. p. 150°.

Attempts to methylate the base, using (i) methyl sulphate and sodium hydroxide, (ii) diazomethane or nitrosomethylurethane and alcoholic potassium hydroxide, were unsuccessful, as were all attempts to acetylate the base by boiling with potassium acetate and acetic anhydride or by other means. The stability of the base is shown by the fact that it may be fused with potassium hydroxide at 180° without decomposition.

7-*Demethylomethylpapaverine* (IX).—Anhydro-7-demethylomethylpapaverinol (10 g.), dissolved in alcohol (70 c.c.) and concentrated hydrochloric acid (70 c.c.), was boiled with a large excess of tin for 3 hours. The pale yellow solution was diluted and allowed to remain over-night. The tin double chloride which had separated was washed, dissolved in boiling aqueous alcohol saturated with hydrogen sulphide, the filtrate concentrated, and the base precipitated by ammonia and crystallised from alcohol, from which it separated in colourless needles, m. p. 148° [Found: C, 70·6; H, 6·4; OMe, 28·0. $C_{20}H_{21}O_4N$ (containing 3MeO) requires C, 70·8; H, 6·2; MeO, 27·4%].

7-Demethylomethylpapaverine dissolves readily in dilute mineral acids, but the salts were not obtained crystalline; the picrate, chromate, platinichloride and aurichloride are yellow precipitates which become oily under boiling water. A nitrosoamine could not be obtained by the addition of sodium nitrite to the solution of the base in dilute hydrochloric acid.

Attempts to methylate the base by means of diazomethane or methyl sulphate and sodium hydroxide were unsuccessful, as were also attempts to acetylate the base by boiling with acetic anhydride and potassium acetate.

As the base has almost the same melting point as, and other properties similar to, those of anhydro-7-demethylomethylpapaverinol, a mixed melting-point determination was made; it showed a large depression.

7-Demethylomethyltetrahydropapaverine (VIII).—The reduction either of 7-demethylopapaverinol (VI) or of the anhydro-base (VII) with tin and hydrochloric acid yielded 7-demethylomethyltetrahydropapaverine, presumably owing to the conversion of the former into the anhydro-base under the influence of the concentrated hydrochloric acid employed. The anhydro-base (VII) was boiled in alcoholic solution with tin and hydrochloric acid exactly as described in the preparation of 7-demethylomethylpapaverine (p. 1458). After 12 hours, the solution was almost colourless and, on pouring into water, a tin double salt separated which was decomposed in the usual manner. The base, precipitated as a slime by the addition of sodium hydroxide, was crystallised from aqueous alcohol when long, slender needles, m. p. 64—65°, were obtained (yield about 25%) [Found: C, 69·8; H, 7·1; N, 4·0; MeO, 27·5. $C_{20}H_{25}O_4N$ (containing 3 MeO) requires C, 70·0; H, 7·3; N, 3·9; MeO, 27·1%].

The base dissolves readily in dilute acids and is slowly converted into a carbonate on exposure to air. The *picrate* separates in orange needles from alcohol, darkens at 210°, and melts with decomposition at 225°. The *nitrosoamine* was prepared by dissolving the base in dilute hydrochloric acid and adding sodium nitrite. The sticky precipitate soon hardens and crystallises from methyl alcohol in long, colourless needles, m. p. 124°, which give the Liebermann reaction (Found: N, 7·8. $C_{20}H_{24}O_5N_2$ requires N, 7·5%).

7-Demethylo-ψ-corydaline (X).—In preparing this base, 7-demethylomethylpapaverine (3 g.), dissolved in concentrated hydrochloric acid (15 c.c.) and water (15 c.c.), was heated on the steam-bath under reflux for 1 hour during the gradual addition of methylal (10 c.c.). The clear solution was cooled, diluted with an equal volume of water, made alkaline with sodium hydroxide, and the precipitate collected. This crude base was dissolved in a little methyl alcohol, much ether added, the alcohol removed by washing three times with water, the ethereal solution dried over potassium carbonate, filtered, and allowed to evaporate slowly. Small prisms gradually separated and then the mother-liquor from these deposited an amorphous base (A). After recrystallising from methyl alcohol, the prisms melted at 150—151° [Found: C, 70·6, 70·9; H, 7·1, 7·0;

MeO, 25·2. $C_{21}H_{25}O_4N$ (containing 3MeO) requires C, 71·0; H, 7·0; MeO, 26·2%]. 7-Demethylo-ψ-corydaline is readily soluble in dilute acids, but does not dissolve in alkalis; if, however, it is shaken for some time with dilute sodium hydroxide and carbon dioxide is passed through the filtered solution, a small amount of an amorphous base (B) separates. Attempts to obtain an acetyl derivative by boiling with acetic anhydride and potassium acetate were unsuccessful, the base being recovered unchanged on the addition of sodium hydroxide. It was also not found possible to methylate the base by treatment with diazomethane or nitrosomethylurethane and alcoholic potassium hydroxide. When methylation was attempted with methyl sulphate and potassium hydroxide or with methyl iodide and silver hydroxide, quaternary ammonium salts of the original base were obtained. The *methiodide* was prepared by boiling the base with excess of methyl iodide for an hour, removing the excess by distillation, and dissolving the residue in boiling water, when, on cooling, the methiodide separated in colourless, hexagonal prisms, m. p. 250° [Found: C, 53·6; H, 5·8; MeO, 19·0. $C_{22}H_{28}O_4NI$ (containing 3MeO) requires C, 53·1; H, 5·7; MeO, 18·2%]. The same methiodide was obtained by boiling the amorphous bases (A) and (B) with methyl iodide. The methochloride, prepared by digesting the methiodide with water and silver chloride, is very soluble and was obtained in small, colourless cubes, m. p. 253° (decomp.), by adding ether to the alcoholic solution. The hydriodide, prepared by adding potassium iodide to the solution of the base in dilute hydrochloric acid, crystallises from water in short, colourless needles, m. p. 242°.

The Dihydro-7-demethylo-ψ-dehydrocorydalinium Salts.—When the solution of 7-demethylo-ψ-corydaline (X) in alcohol containing potassium acetate is heated to boiling and an alcoholic solution of iodine gradually added, a sparingly soluble periodide separates in long, brown needles, m. p. 210°. The suspension of this in hot water is decomposed by sulphur dioxide and the yellow solution, on cooling, deposits small, yellow needles of *dihydro-7-demethylo-ψ-dehydrocorydalinium iodide*, m. p. 250° (Found: C, 52·6; H, 5·3. $C_{21}H_{24}O_4NI$ requires C, 52·4; H, 5·0%). The same iodide was obtained from nor-ψ-corydaline by oxidising it with a large excess of mercuric acetate under the conditions described by Perkin (J., 1918, **113**, 515) in the preparation of the *epi*berberinium salts from tetrahydro*epi*berberine. After removal of the mercurous acetate, the acetic acid solution was diluted with water, saturated with hydrogen sulphide, and the filtrate concentrated and mixed with potassium iodide, when, on cooling, the iodide separated in yellow needles, m. p. 250°. No depression was observed when this was mixed with the specimen of the iodide prepared by the iodine

oxidation process described above. The *chloride* was obtained by decomposing the aqueous solution of the iodide with silver chloride, removing the silver salts, and concentrating the filtrate, when the chloride separated in small, yellow needles, m. p. 235° (decomp.) (Found: C, 64·5; H, 6·3. $C_{21}H_{24}O_4NCl$ requires C, 64·7; H, 6·2%). This chloride dissolves in concentrated sulphuric acid to a yellow solution which becomes brilliant emerald-green on adding a crystal of sodium nitrate; after a few minutes, the colour changes to bright red.

Keto-7-demethylo-ψ-corydaline (XIII).—This substance is obtained when the chloride (see above) is boiled with a large excess of potassium hydroxide (50%) for 4 hours; after standing over-night, the mixture of yellow crystals and brown resin is collected, ground, and extracted several times with boiling dilute hydrochloric acid. The insoluble residue is crystallised first from alcohol and then from acetic acid, from which the keto-derivative separates in long, colourless prisms, m. p. 210° (Found: C, 68·1; H, 6·3. $C_{21}H_{23}O_5N$ requires C, 68·3; H, 6·2%).

Keto-7-demethylo-ψ-corydaline has many properties in common with oxyberberine. It is sparingly soluble in the usual organic solvents except glacial acetic acid and is devoid of basic properties. The solution in concentrated sulphuric acid is yellow and becomes emerald-green and finally deep purple on the addition of a crystal of sodium nitrate. Attempts to methylate this keto-derivative by boiling with methyl sulphate and sodium hydroxide in alcoholic solution and also by means of diazomethane or to acetylate it by boiling with acetic anhydride and sodium acetate for 3 hours were unsuccessful, the substance being recovered in each case.

The acid-soluble portion of the product of the action of potassium hydroxide on 7-demethylo-ψ-corydalinium chloride contained much unchanged chloride. It was heated on the steam-bath, and excess of ammonia added, when an oil was precipitated which rapidly solidified. This substance separated from alcohol in small prisms, melted at 150—151°, and was identified as 7-demethylo-ψ-corydaline (X) by the mixed melting point and by conversion into the methiodide, m. p. 250°.

Anhydro-7-demethylomethyl-ψ-corydaline (XIII).—This substance was obtained when a concentrated aqueous solution of the methochloride of 7-demethylo-ψ-corydaline (p. 1460) was boiled with a large excess of potassium hydroxide for 6 hours. The oil which had separated was extracted with ether, the ethereal extract dried over potassium carbonate, and the solvent evaporated, when a gum remained which hardened to a resin, but could not be obtained crystalline.

The base was dissolved in dilute hydrochloric acid, the solution

evaporated to dryness under diminished pressure, and the residue dissolved in methyl alcohol. On the addition of ether, the hydrochloride separated in small needles, m. p. 228° (decomp.) (Found: C, 65·0; H, 7·1. $C_{22}H_{28}O_4NCl$ requires C, 65·1; H, 6·9%). The hydriodide, obtained by the addition of potassium iodide to the aqueous solution of the hydrochloride, separates from water in small needles, m. p. 232°. The *picrate*, prepared by the addition of picric acid to the alcoholic solution of the base, crystallises from alcohol in long, yellow needles which froth to a turbid liquid at 130°, melt completely at 165°, and evidently contain alcohol of crystallisation (Found: C, 55·7; H, 6·2; N, 8·3. $C_{28}H_{30}O_{11}N_4,2C_2H_6O$ requires C, 55·7; H, 6·1; N, 8·1%).

The authors desire to thank the Research Fund Committee of the Chemical Society and the Government Grant Committee of the Royal Society for grants which have defrayed much of the expense of these researches. One of us (R.D.H.) wishes to express his gratitude to the Commissioners of the 1851 Exhibition for a Scholarship which has enabled him to participate in these researches. We wish also to thank Mr. Fred Hall for carrying out the whole of the analyses contained in the four parts of this investigation.

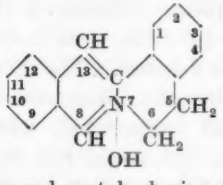
THE DYSON PERRINS LABORATORY,
OXFORD. [*Received, April 28th*, 1925.]

CXCVIII.—*Synthesis of* 2:3:10:11-*Bismethylenedioxyprotoberberine and* 6:7:3′:4′-*Bismethylenedioxyprotopapaverine.**

By JOHANNES SYBRANDT BUCK, WILLIAM HENRY PERKIN, jun., and THOMAS STEVENS STEVENS.

DURING the course of experiments which led to the synthesis of *ψ-epi*berberine (Buck and Perkin, J., 1924, **125**, 1675), a parallel

* The nomenclature of the substances obtained during the course of this investigation, and of other investigations which are in progress, has caused considerable difficulty, and it is suggested, with the concurrence of the Editor, that the parent substances of berberine and papaverine,



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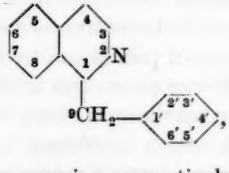
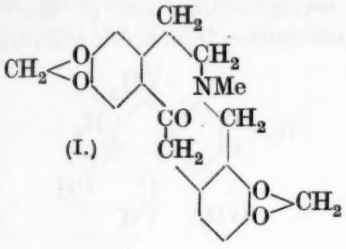
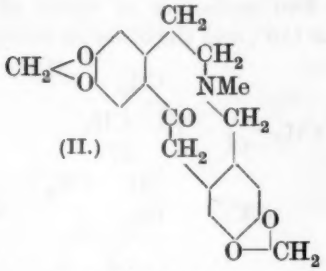


should be named protoberberine and protopapaverine, respectively.

investigation was undertaken with a view to prepare substances bearing the same relation to protopine as *epi*berberine and its derivatives bear to cryptopine. It was, of course, expected at that time that the products obtained would be related to protopine (I), and not to ψ-protopine (II), but, although we have as yet no direct proof of this, there can be little doubt that these substances are of the type (II).

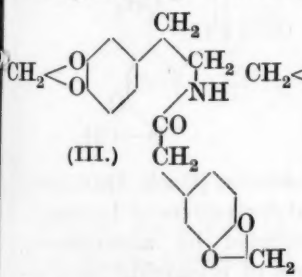


(I.)

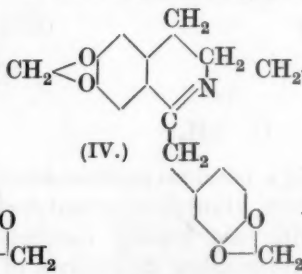


(II.)

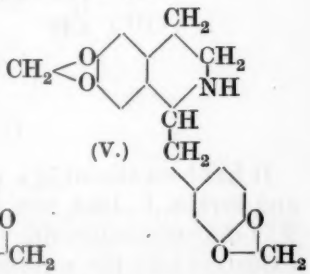
The synthesis was carried out on lines similar to those which had led to the preparation of ψ-*epi*berberine (Buck and Perkin, *loc. cit.*) and of ψ-berberine (Haworth, Perkin, and Rankin, J., 1924, **125**, 1686). Homopiperonoylhomopiperonylamine (III), which had previously been described by Decker (*Annalen*, 1913, **395**, 282), was prepared by heating together homopiperonylamine and homopiperonylic acid, and transformed, by boiling with phosphorus oxychloride in toluene solution, into 6 : 7 : 3′ : 4′-*bismethylenedioxy*-3 : 4-*dihydroprotopapaverine* (IV), a crystalline substance (m. p. 92—96°) which rapidly oxidises in the air to the corresponding ketone. The substance (IV) is reduced smoothly by means of zinc dust and dilute sulphuric acid to 6 : 7 : 3′ : 4′-*bismethylenedioxy*-1 : 2 : 3 : 4-*tetrahydroprotopapaverine* (V).



(III.)



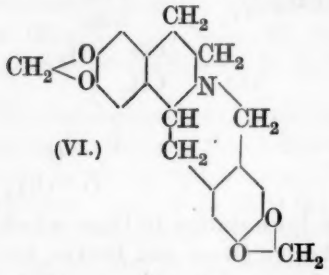
(IV.)



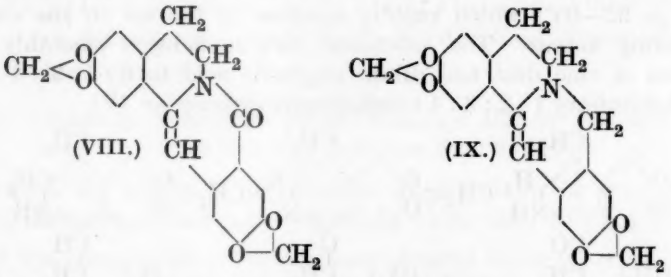
(V.)

By successive treatment with formaldehyde and hydrochloric acid, the tetrahydro*iso*quinoline is converted, no doubt through its *N*-hydroxymethyl derivative, into the hydrochloride of 2 : 3 : 10 11-*bismethylenedioxytetrahydroprotoberberine* (VI). This base resembles its analogues, tetrahydro-ψ-berberine (m. p. 177°)

and tetrahydro-ψ-*epi*berberine (m. p. 160—161°) in most of its properties, but differs noticeably in its high melting point (214°) and its comparative insolubility in alcohol. It is readily oxidised by iodine in presence of sodium acetate, with the formation of 2 : 3 : 10 : 11-*bismethylenedioxyprotoberberinium iodide* (VII), which is converted into the corresponding *chloride* by digestion with water and silver chloride. This chloride crystallises from hot water with two molecules of water of crystallisation, one of which is lost at 110°, and the other on recrystallisation from acetic anhydride.

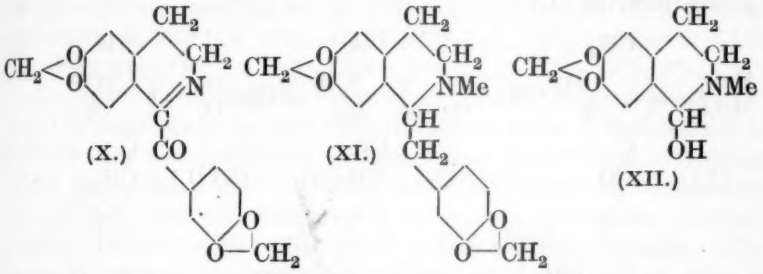


On treatment with hot sodium hydroxide solution, this quaternary chloride undergoes a transformation in the same manner as berberinium chloride, yielding a mixture of 2 : 3 : 10 : 11-*bismethylenedioxyoxyprotoberberine* (VIII), analogous to oxyberberine, and 2 : 3 : 10 : 11-*bismethylenedioxydihydroprotoberberine* (IX), corresponding to dihydroberberine.

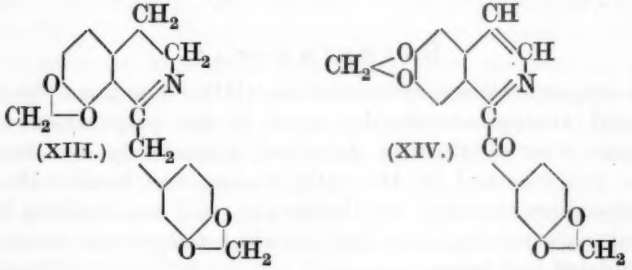


It has been shown in a previous communication (Buck, Haworth, and Perkin, J., 1924, **125**, 2176) that several derivatives of 1-benzyl-3 : 4-dihydro*iso*quinoline are readily converted by atmospheric oxidation into the corresponding derivatives of benzoyldihydro*iso*quinoline, and the substance (IV) behaves in perfectly analogous fashion. On exposure of its alcoholic solution to the air for a few days, it is oxidised to 6 : 7 : 3′ : 4′-*bismethylenedioxy*-9-*keto*-3 : 4-*dihydroprotopapaverine* (X), which crystallises in long needles melting at 136°, and, like the analogous substances previously examined, forms

yellow salts and gives an emerald-green coloration on boiling with acetic anhydride. It is worthy of note that Decker, Kropp, Hoyer, and Becker (*Annalen*, 1913, **395**, 299) treated homopiperonoylhomopiperonylamine with phosphorus oxychloride and isolated a picrate which gave on decomposition a substance melting at 136—137° and forming yellow salts. It would seem highly probable that the compound obtained by these authors, to which they attributed the structure (IV), is really identical with (X).

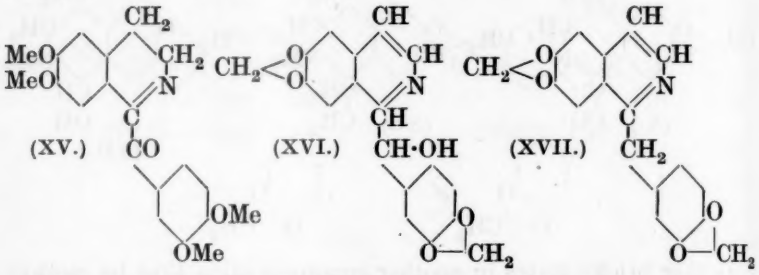


Decker briefly states in another communication that by methylation and reduction of this product he obtained a tetrahydro*iso*quinoline derivative (XI), which gave on oxidation piperonal and hydrastinine (XII), a result which proves that, as was to be expected, the action of phosphorus oxychloride on homopiperonoylhomopiperonylamine takes the course indicated and does not lead to the isomeric 7 : 8 : 3′ : 4′-bismethylenedioxy-1 : 2 : 3 : 4-tetrahydroprotopapaverine (XIII).



When the ketone (X) is boiled with methyl-alcoholic potassium hydroxide solution, it is rapidly oxidised with production of 6 : 7 : 3′ : 4′-*bismethylenedioxy*-9-*ketoprotopapaverine* (XIV), a weakly basic substance, which, like papaveraldine, forms yellow salts. Stuchlik (*Monatsh.*, 1900, **21**, 814), without giving any experimental details, states that Goldschmiedt obtained papaverine by reducing papaveraldine with zinc dust and acetic anhydride. With the ultimate object of applying the method to the substance (XIV), we

made repeated attempts, under various conditions, to carry out this reaction, but it was not found possible to obtain a satisfactory yield of papaverine, and, owing to the inaccessibility of the compound (XIV), it was necessary to devise a more suitable process. Since the tetrahydro*iso*quinoline derivative (V) is comparatively easily obtainable, an attempt was made to oxidise the analogous tetrahydropapaverine by means of iodine, but the main product of the reaction was 6 : 7 : 3′ : 4′-*tetramethoxy*-9-*keto*-3 : 4-*dihydroprotopapaverine* (XV).



Ultimately it was found that papaverinol could be readily converted into papaverine by the action of an acetic acid solution of hydrogen bromide, followed by reduction with zinc dust. The substance (XIV) was then reduced with zinc dust and acetic acid to give the papaverinol analogue, 6 : 7 : 3′ : 4′-*bismethylenedioxy*-9-*hydroxyprotopapaverine* (XVI), which was then further reduced in the manner just described, and yielded the required 6 : 7 : 3′ : 4′-bismethylenedioxyprotopapaverine (XVII).

Experimental.

Homopiperonoylhomopiperonylamine (III).—The homopiperonylic acid and homopiperonylamine used in the preparation of this substance were obtained as described, respectively, by Buck and Perkin (*loc. cit.*) and by Haworth, Perkin, and Rankin (*loc. cit.*). The procedure employed by Decker (*loc. cit.*) was modified in that the materials were heated at 190°, at which temperature the reaction is completed in 2 hours.

6 : 7 : 3′ : 4′-*Bismethylenedioxy*-3 : 4-*dihydroprotopapaverine* (IV).—Homopiperonoylhomopiperonylamine (45 g.), toluene (225 c.c.), and phosphorus oxychloride (90 c.c.) are boiled under reflux for 15 minutes. On cooling, the mixture is diluted with light petroleum, and after a few minutes the supernatant liquid is decanted from the light brown gum. After washing thoroughly with ether, the gum is dissolved in aqueous alcohol, and, on addition of ether, the solution deposits a cream-coloured phosphate, which is

recrystallised from alcohol–ether. The salt is dissolved in dilute alcohol, treated with excess of potassium hydroxide solution, and water cautiously added, when the free base separates in nearly colourless needles, m. p. 92—96° (Found : C, 69·4; H, 4·8; N, 4·2. $C_{18}H_{15}O_4N$ requires C, 69·9; H, 4·9; N, 4·5%). The substance could not be further purified, as it oxidised quickly in the air. It is readily soluble in alcohol, and dissolves in dilute acids with a pale yellow colour. The *picrate* separates from alcohol–acetic acid in pale yellow needles, m. p. 220° (blackening and effervescence) (Found : C, 53·9; H, 3·6. $C_{18}H_{15}O_4N,C_6H_3O_7N_3$ requires C, 53·5; H, 3·4%).

6 : 7 : 3′ : 4′-*Bismethylenedioxy*-1 : 2 : 3 : 4-*tetrahydroprotopapaverine* (V).—In the preparation of this substance it is unnecessary to isolate the last-mentioned product. The brown gum remaining after decantation of the toluene and light petroleum is dissolved in alcohol, treated with excess of sodium hydroxide solution, largely diluted with water, and extracted with benzene. The benzene extract is shaken with dilute sulphuric acid (a litre of 10—15%), and the acid layer reduced on the steam-bath with a considerable excess of zinc powder. During the reaction, the product separates as sulphate, and is redissolved by boiling the liquid, which is then filtered, rendered strongly alkaline with sodium hydroxide solution, and extracted with ether. On standing, the ethereal extract deposits the tetrahydro-derivative in large crystals, m. p. 84—85°, the yield being 70—75% of that theoretically obtainable from the original homopiperonoylhomopiperonylamine (Found : C, 69·5; N, 5·6; N, 4·1. $C_{18}H_{17}O_4N$ requires C, 69·4; H, 5·5; N, 4·5%). The substance (V) is readily soluble in the usual organic solvents, and tends to separate from them as an oil. It dissolves in dilute acids to form colourless, rather sparingly soluble salts, and in concentrated sulphuric acid to give a dark yellow solution, which turns reddish-brown on addition of a crystal of potassium nitrate. From solutions of the hydrochloride, potassium iodide precipitates the *hydriodide* as a gum, which solidifies on scratching, and crystallises from much hot water in groups of small, white needles, m. p. 250—254°. The *picrate* crystallises from alcohol–acetic acid in minute, bright orange needles, which soften at 190° and melt with decomposition at 210° (Found : C, 53·3; H, 4·1. $C_{18}H_{17}O_4N,C_6H_3O_7N_3$ requires C, 53·3; H, 3·7%).

2 : 3 : 10 : 11-*Bismethylenedioxytetrahydroprotoberberine* (VI).—The last-mentioned base (6 g.) is dissolved in boiling methyl alcohol (30 c.c.), and sodium bicarbonate (3 g.) and formalin (10 c.c. of 40%) are successively added. After warming for a short time, the liquid is diluted, and the white gum which separates completely

is precipitated by addition of sodium chloride, washed free from formaldehyde, and dissolved in hot concentrated hydrochloric acid (40 c.c.). The white hydrochloride which crystallises on cooling is collected, dissolved in hot aqueous alcohol, and treated with ammonia, when the base separates in small, white needles. A further quantity may be obtained from the acid mother-liquors, making a total yield of 80% of theory. In some experiments, the hydrochloride was obtained in a highly insoluble form, which, however, gave the same base on decomposition. Bismethylenedioxytetrahydroprotoberberine crystallises from much alcohol in small, white needles, m. p. 214° (Found: C, 70·7; H, 5·4; N, 4·1. $C_{19}H_{17}O_4N$ requires C, 70·6; H, 5·3; N, 4·3%). This substance, which slowly turns brown in the air, is rather sparingly soluble in alcohol or acetone, but more readily soluble in benzene and especially in chloroform. It dissolves readily in cold acetic acid and slowly separates if the solution be diluted with water or alcohol. With dilute mineral acids it forms stable, rather sparingly soluble salts; when concentrated sulphuric acid is added to a solution of the base in acetic acid, a yellow solution is obtained, which turns red on addition of a crystal of potassium nitrate.

2 : 3 : 10 : 11-*Bismethylenedioxyprotoberberinium Iodide* (VII).—The tetrahydro-compound (VI) (25 g.) and sodium acetate (80 g.) are dissolved in hot alcohol (700 c.c.), with the addition of sufficient acetic acid to bring about solution, and iodine (40 g.), dissolved in alcohol, is gradually added. The iodine is rapidly absorbed, and the quaternary iodide soon separates as a yellow powder, which is collected on cooling: the yield is 30 g. This highly insoluble salt crystallises in small, bright yellow rods, which have an intensely bitter taste and decompose without melting above 300°. The corresponding *chloride* is obtained by digesting the iodide on the steam-bath with a slight excess of silver chloride and 40 parts of water for 2 hours and filtering hot from the silver salts, when the chloride separates on cooling in bright yellow needles which may be recrystallised from dilute hydrochloric acid. The air-dried salt has the composition $C_{19}H_{14}O_4NCl,2H_2O$, and loses $1H_2O$ at 110° (Found: loss at 110°, 4·2; Cl, 9·3. $C_{19}H_{14}O_4NCl,2H_2O$ requires loss, 4·6; Cl, 9·1%. The salt dried at 110° gave C, 61·1; H, 4·4. $C_{19}H_{14}O_4NCl,H_2O$ requires C, 61·0; H, 4·3%). When the substance is recrystallised from acetic anhydride, in which it is moderately soluble, it separates in the anhydrous condition in pale yellow needles, which decompose above 300° and dissolve in concentrated sulphuric acid to a pale yellow solution (Found: C, 64·0; H, 4·0. $C_{19}H_{14}O_4NCl$ requires C, 64·1; H, 3·9%). The *picrate* is obtained by adding excess of aqueous picric acid to a hot solution of the

chloride, and recrystallising the precipitate from a large quantity of acetic acid, from which it separates in bright orange-yellow needles, which darken above 260° and explode at 310° (Found : C, 54·7; H, 2·9. $C_{19}H_{14}O_4N,C_6H_2O_7N_3$ requires C, 54·7; H, 3·1%). It is noteworthy that this salt separates in the anhydrous condition, whilst the analogous berberinium, *ψ*-berberinium, and *ψ-epi*berberinium picrates contain an additional molecule of water.

2 : 3 : 10 : 11-*Bismethylenedioxyoxyprotoberberine* (VIII) *and* 2 : 3 : 10 : 11-*Bismethylenedioxydihydroprotoberberine* (IX).—The quaternary chloride (5 g.) is dissolved in boiling water (150 c.c.), added to potassium hydroxide solution (100 c.c. of 40%), and the mixture heated at 100°. The brown gum, which separates, soon solidifies, and is then ground up and the heating continued for 3 hours. After cooling, the solid is collected, washed with water, finely powdered, and extracted three times with hot dilute hydrochloric acid (80 c.c. of 2*N* in all). The residue is dissolved in hot acetic acid, and *bismethylenedioxyoxyprotoberberine* separates on cooling in fine, pale yellow needles, which are very insoluble in most organic solvents except acetic acid, and melt above 270° : the yield is about 2 g. (Found : C, 68·2; H, 3·9; N, 4·3. $C_{19}H_{13}O_5N$ requires C, 68·1; H, 3·9; N, 4·2%). The substance is insoluble in dilute mineral acids, and, unlike oxyberberine and oxy*epi*berberine, separates from acetic acid in the free state, and not as acetate. Its solution in 50% sulphuric acid turns brownish-violet on addition of a drop of concentrated nitric acid.

When the united hydrochloric acid extracts, obtained as described above, are cooled to 0°, they deposit yellow crystals, which are then dissolved in hot water and treated with excess of ammonia; and the brown gum, which separates and soon solidifies, is collected. This material is extracted with much acetone and the extract concentrated, when some brown solid separates on standing. The filtrate from this solid is then warmed, and, after a little water has been added, deposits, on cooling, bright yellow leaflets of *bismethylenedioxydihydroprotoberberine* (0·7 g.) (Found : C, 71·2; H, 5·0; N, 4·6. $C_{19}H_{15}O_4N$ requires C, 71·0; H, 4·7; N, 4·4%). The base melts at 161—164°, and dissolves readily in acetone to a bright yellow solution with a green fluorescence. With strong sulphuric acid, it forms a dark yellow solution which turns reddish-brown on addition of a crystal of potassium nitrate. The *picrate* separates from acetic acid, in which it is sparingly soluble, in small golden-brown prisms, which gradually darken and decompose above 240° (Found : C, 54·5; H, 3·3. $C_{19}H_{15}O_4N,C_6H_3O_7N_3$ requires C, 54·5; H, 3·2%).

6 : 7 : 3′ : 4′-*Bismethylenedioxy*-9-*keto*-3 : 4-*dihydroprotopapaverine* (X).—The substance (IV) is dissolved in ether–methyl alcohol and exposed to the air for 10 days, the solvents being renewed at intervals. The product is dissolved in methyl alcohol, with the addition of a little hydrochloric acid, and rendered alkaline with ammonia, when crystals are deposited, along with tarry matter, which renders their purification rather tedious. After recrystallising several times from methyl alcohol, the base forms long, colourless needles, m. p. 136° (Found: C, 67·3; H, 4·5; N, 4·1. $C_{18}H_{13}O_5N$ requires C, 66·9; H, 4·0; N, 4·3%). The substance is readily soluble in the usual solvents, and dissolves in dilute acids to give bright yellow salts, which are mostly easily soluble. Its solution in acetic anhydride turns emerald-green on boiling. The *hydriodide* is precipitated when solid potassium iodide is added to a solution of the hydrochloride, and separates from alcohol–ether in minute, yellow prisms, m. p. 216—219° (decomp.), which are fairly soluble in hot alcohol. The *picrate* crystallises from alcohol–acetic acid in minute, orange-yellow plates, m. p. 202° (decomp.; softening above 180°) (Found: C, 52·6; H, 3·3. $C_{18}H_{13}O_5N,C_6H_3O_7N_3$ requires C, 52·2; H, 2·9%). The *oxime* is obtained by heating a mixture of the base (0·5 g.), pyridine (4 c.c.), alcohol (1 c.c.), and hydroxylamine hydrochloride (0·15 g.) on the water-bath for 2 hours. On diluting the mixture with water and saturating with carbon dioxide, a white solid is precipitated, which is recrystallised from methyl alcohol. This oxime forms a white powder, m. p. 235° (decomp.), which is sparingly soluble in the usual organic solvents and dissolves in concentrated sulphuric acid with an orange colour (Found: C, 64·0; H, 3·9. $C_{18}H_{14}O_5N_2$ requires C, 63·9; H, 4·1%).

6 : 7 : 3′ : 4′-*Bismethylenedioxy*-9-*ketoprotopapaverine* (XIV).—The base (X) (3 g.) is heated on the steam-bath for ½ hour with 10% methyl-alcoholic potassium hydroxide (30 c.c.). After cooling, the solid is collected and recrystallised from alcohol, from which it separates in fine, colourless needles, m. p. 186° (yield 50%) (Found: C, 61·2; H, 3·4; N, 4·5. $C_{18}H_{11}O_5N$ requires C, 67·3; H, 3·4; N, 4·4%). The substance is moderately soluble in hot alcohol, and readily soluble in acetic acid, from solutions in which it separates at once on dilution with water. It dissolves readily in dilute mineral acids, forming yellow salts, and in concentrated sulphuric acid to a deep orange-red solution. On boiling with acetic anhydride, a pale green liquid is produced. When potassium iodide is added to a solution of the base in dilute hydrochloric acid, the sparingly soluble *hydriodide* separates in minute, yellow prisms, which are completely hydrolysed by hot water, darken above 210°, and melt with decomposition at about 230°. The *picrate* is pre-

pared in alcoholic solution, and crystallises from alcohol–acetic acid in well-defined, short, yellow prisms, m. p. 240° (decomp.) (Found : C, 52·6; H, 2·6. $C_{18}H_{11}O_5N,C_6H_3O_7N_3$ requirees C, 52·4; H, 2·5%). The *oxime* is obtained by heating the base (0·5 g.) with hydroxylamine hydrochloride (1·5 g.) and potassium acetate (2 g.) in alcoholic solution on the steam-bath for 8 hours. The liquid is then filtered, concentrated, and slightly diluted with water, when the oxime separates on cooling as a white powder, which crystallises from alcohol in minute, transparent laminæ, melting with blackening and effervescence at about 275° (Found : C, 63·9; H, 3·9; N, 8·2. $C_{18}H_{12}O_5N_2$ requires C, 64·3; H, 3·6; N, 8·3%). It is rather sparingly soluble in the ordinary solvents.

6 : 7 : 3′ : 4′-*Bismethylenedioxy*-9-*hydroxyprotopapaverine* (XVI. Compare Stuchlik, *Monatsh.*, 1900, **21**, 814).—The ketone (XIV) (1 g.) is dissolved in acetic acid (10 c.c.), and reduced on the steam-bath with a moderate excess of zinc powder, added during 3 hours. The hot liquid is filtered, the residue washed with hot water, and the filtrate diluted to 100 c.c.; no appreciable quantity of unaltered material separates on standing. The zinc is precipitated by means of hydrogen sulphide, the filtrate concentrated on the steam-bath, nearly neutralised with solid sodium carbonate, rendered strongly alkaline with ammonia, and extracted with chloroform. After removing the chloroform, the residue is recrystallised from benzene, from which it separates in short, colourless prisms, m. p. 169—170° (Found : C, 66·6; H, 4·3. $C_{18}H_{13}O_5N$ requires C, 66·9; N, 4·0%). The base is moderately soluble in alcohol or benzene, very sparingly soluble in light petroleum, and dissolves in concentrated sulphuric acid to give a deep bluish-violet solution, which turns yellowish-brown on addition of a crystal of potassium nitrate. Its salts, like those of papaverinol, are fairly soluble in water and do not crystallise readily.

6 : 7 : 3′ : 4′-*Bismethylenedioxyprotopapaverine* (XVII).—The substance (XVI) is dissolved in 10—20 parts of acetic acid, saturated with hydrogen bromide, and allowed to remain for 12 hours The solution is then warmed to 25°, stirred mechanically, and reduced during 1—1½ hours with a considerable excess of zinc powder, the reaction being completed by warming at 50°. The liquid is then diluted, rendered strongly alkaline with ammonia, and extracted with chloroform. After evaporating the chloroform, the base is recrystallised from benzene, and separates in small balls of needles, m. p. 170—172°, which give an intense bluish-violet coloration with concentrated sulphuric acid (Found : C, 70·3; H, 4·6. $C_{18}H_{13}O_4N$ requires C, 70·4; H, 4·2%). The *picrate* separates slowly from alcohol in minute, pale yellow prisms, m. p. 199—202° (decomp.).

The conversion of papaverinol into papaverine is readily carried out by the method just described: during the reduction, a highly insoluble double zinc bromide separates, which is collected, dissolved in much boiling water, and treated with excess of ammonia, and the base then isolated in the usual manner.

Oxidation of Tetrahydropapaverine.—This base, prepared as described by Pyman (J., 1909, **95**, 1614), and an excess of sodium acetate were dissolved in alcohol on the steam-bath, and iodine (slightly more than 4 atoms) was added in alcoholic solution during 3 hours. The iodine was at first rapidly absorbed, and the solution became dark brown. After being treated with sulphur dioxide and most of the alcohol removed by evaporation, the liquid was diluted with water, rendered alkaline with ammonia, and extracted with chloroform. The chloroform extract was washed with dilute hydrochloric acid, which removed very little material, and on concentrating the chloroform solution, yellow crystals of the hydrochloride of a base melting at 190—191° were obtained. The substance gave a green solution on boiling with acetic anhydride, and no depression in melting point was observed on mixing with a specimen of 6 : 7 : 3′ : 4′-tetramethoxy-9-keto-3 : 4-dihydroprotopapaverine (XV), prepared by Buck, Haworth, and Perkin (*loc. cit.*) by the atmospheric oxidation of the corresponding benzyldihydro*iso*quinoline. Concentration of the chloroform mother-liquors from this hydrochloride gave small quantities of two scarcely basic substances, melting at 300° and 163—167°, which were not farther examined.

One of us (T. S. S.) wishes to thank the Ramsay Memorial Trustees for a Fellowship which has enabled him to take part in this investigation and another (W. H. P.) is indebted to the Government Grant Committee of the Royal Society for a grant from the Research Fund.

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OXFORD. [*Received, April 29th*, 1925.]

CXCIX.—*Alcohols of the Hydroaromatic and Terpene Series. Part IV. α- and β-Fenchyl Alcohols and some Esters derived therefrom.*

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WHEN *d*-fenchone is reduced, a mixture of two isomeric fenchyl alcohols is produced. Each of these alcohols when isolated in an optically pure condition exhibits lævorotation and on oxidation

regenerates a ketone which is identical with the *d*-fenchone from which it was obtained. These fenchyl alcohols must therefore be stereoisomerides; a view which is in harmony with stereochemical considerations of the fenchone molecule and also with the general behaviour of optically active cyclic ketones on reduction. For example, it has been shown in Part II * of this series that *l*-menthone on reduction gives a mixture of *l*-menthol and *d-neo*menthol and in Part I that *d*-camphor on reduction gives a mixture of *d*-borneol and *l-iso*borneol, and further, using the same method, Tschugaev (*Ber.*, 1912, **45**, 1293) showed that tanacetone on reduction yields two tanacetyl alcohols of opposite, but unequal, rotatory powers.

Although these two fenchyl alcohols possess the same sign of rotation and thus differ from the other pairs mentioned above, yet in some respects they show rotatory effects of an opposite character, as will be seen from the following table of the rotatory powers of α- and β-fenchyl alcohols and some of their esters.

Specific Rotatory Power, $[\alpha]^{20°}_{5461}$.

	Homogeneous.	Ethyl alcohol.	Carbon disulphide.
α-Fenchyl alcohol	−15·04°	−15·37°	− 6·70°
β- „ „	−27·97	−26·23	−38·27
α- „ formate	−80·67	−86·50	−72·51
β- „ „	−12·88	−11·74	−15·79
α- „ acetate	−75·73	—	—
β- „ „	−16·90	—	—
α- „ *p*-nitrobenzoate	—	—	−23·2
β- „ „	—	—	+13·5
α- „ hydrogen phthalate	—	+27·0	—
β- „ „ „	—	+13·3	—

A further example of this behaviour is found in the temperature–rotation curves of the α- and the β-alcohols: that for the β-alcohol reaches a maximum and then falls slowly, whilst that for the α-alcohol falls to a minimum and then rises.

In each case, conversion of α-fenchyl alcohol into a neutral ester has given a compound which possesses a considerably higher lævorotatory power than the alcohol from which it was derived, whilst the conversion of β-fenchyl alcohol into neutral esters yields compounds which possess considerably lower lævorotatory powers than the parent alcohol—in one case, that of the *p*-nitrobenzoate, the sign of rotation has become positive. There is, however, an anomaly in the case of the hydrogen phthalic esters, which both possess dextrorotatory powers. The effect of solvents on rotatory power is in opposite directions in the cases of α- and β-fenchyl alcohols and α- and β-fenchyl formates.

* Part I, J., 1907, **91**, 1979; Part II, J., 1912, **101**, 109.

α-*Fenchyl alcohol* is readily separated from the mixture of alcohols obtained by the reduction of *d*-fenchone by the following method. The mixture of hydrogen phthalates obtained by heating the alcohols with phthalic anhydride is crystallised from acetic acid until a product of constant rotatory power is obtained: this is pure α-fenchyl hydrogen phthalate. The more soluble fractions of the hydrogen phthalates are hydrolysed, and the resulting fenchyl alcohol is converted into the *p*-nitrobenzoate. This ester is crystallised from ethyl alcohol until constancy of rotation is reached: this yields as the less soluble fraction pure β-fenchyl *p*-nitrobenzoate. Hydrolysis of the hydrogen phthalate of constant rotatory power gives pure α-fenchyl alcohol, whilst the *p*-nitrobenzoate yields on hydrolysis pure β-fenchyl alcohol. Details of the various operations involved are recorded in the experimental part. The other esters were prepared by the usual methods.

In view of the general similarity in structure of the camphor and fenchone molecules it was thought that an examination of some simple esters of borneol and of *iso*borneol would throw light on the relations between α- and β-fenchyl alcohols. A number of these have been prepared and their rotatory powers determined both in the homogeneous condition over a wide range of temperature and in solution. This is the first recorded case of the examination of two series of esters derived from *cis*- and *trans*-isomeric alcohols. Under the experimental conditions employed, the esters of both series possess simple rotatory dispersion.

The curve connecting the specific rotatory powers of the bornyl esters is similar in character to that for the corresponding α-fenchyl esters, whilst the curve for the *iso*bornyl esters is similar to that for the corresponding β-fenchyl esters. The temperature–rotation curves of the bornyl esters and the *iso*bornyl esters are similar to those of the α- and the β-fenchyl esters—the rotatory powers in all cases decreasing regularly with rise of temperature.

In general, therefore, the bornyl and *iso*bornyl esters bear much the same relation to each other as do the α- and β-fenchyl esters.

The Relation between the Specific Rotatory Powers of Members of Homologous Series of Esters and the Length of the Acyl Group.

A consideration of the values of the specific rotatory powers of the members of the four homologous series of esters now described affords a good illustration of the complexity of the problem involved in attempting to discover the relations which may exist between chemical constitution and optical activity and of the difficulty of drawing deductions of a general character. When their specific rotatory powers, $[\alpha]_{5461}$, are plotted against the number of carbon

atoms in the growing acyl chain, four different types of curves are obtained which may be briefly described as follows :—

(1) *Bornyl Esters.*—The five esters of this series lie on a smooth curve which falls steadily and fairly rapidly from the first member to the last.

(2) iso-*Bornyl Esters.*—The first member has a relatively very low value : there is then a big jump to the second member, after which the values for the remaining three members fall steadily but slowly.

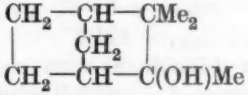
(3) β-*Fenchyl Esters.*—The curve is similar in character to that given by the *iso*bornyl esters except that the relatively low value for the first member of the series is not so pronounced and the values from the second member onwards fall much more rapidly.

(4) α-*Fenchyl Esters.*—These lie on a smooth curve which falls steadily from the first member to the last. There are, however, three notable exceptions—a pronounced exaltation is shown by the propionate and a second pronounced exaltation by the *n*-heptoate and the *n*-octoate. In these three cases the asymmetric carbon atoms (which form part of a ring system) together with the acyclic acyl groups form chains which contain respectively five, nine, and ten atoms, thus : $>CH{-}O{-}\overset{\overset{O}{\|}}{C}{-}CH_2{-}CH_3$.

Stereochemical considerations lead to the view that a chain containing five (and ten) carbon (or carbon and oxygen) atoms would have all but returned on itself and completed one (or two) turn of a spiral.

(For a consideration of similar cases see Pickard, Kenyon, and Hunter, J., 1923, **123**, 1).

One of the most difficult of the unsolved problems in terpene chemistry is the relation between borneol and *iso*borneol. The usually accepted formula of the latter is unsatisfactory in that it represents



the compound as a tertiary alcohol. Numerous attempts have been made in this laboratory to prepare esters of tertiary alcohols by the method which has proved so satisfactory in the case of secondary alcohols, *i.e.*, by heating with acid anhydrides or by treatment with acid chlorides in pyridine solution, but in no single case has an ester been produced in sufficient quantity for isolation; the compound obtained in each case being an unsaturated hydrocarbon. When it is borne in mind that *iso*borneol, heated with phthalic

anhydride at 110—115° for several hours, is quantitatively converted into its hydrogen phthalate, the contrast between the behaviour of this alcohol and of tertiary alcohols as a class is most marked.

Moreover, many attempts have been made to effect the resolution of tertiary alcohols by the methods which have proved so successful in the case of secondary alcohols, but in no single case, as yet, has a tertiary alcohol containing the hydroxyl group attached to the asymmetric carbon atom been resolved. On the other hand, *iso*-borneol is resolved into its *d*- and *l*-forms by this method with the utmost ease and readiness. The results of the investigation here recorded lend support to the view that bornel and *iso*borneol are geometrical isomerides, a result which is also in harmony with the experimental work described in Part I (*loc. cit.*).

Another curious fact is that in the resolution of *cis*- and *trans*-isomerides by the acid-ester method a given alkaloid (as a rule) forms a less soluble salt with the acid ester of the *d*-form of the *cis*-isomeride and with the *l*-form of the *trans*, or *vice versa*. For example, strychnine forms a less soluble salt with the *d*-isomeride of "α" 2-methyl*cyclo*hexanol and with the *l*-isomeride of "β" 2-methyl*cyclo*hexanol: brucine forms a less soluble salt with *l*-menthol and with *d-neo*menthol. Similarly, strychnine (and *l*-menthylamine) forms a less soluble salt with *d-iso*borneol and with *l*-borneol. These results may be regarded as further support for the view that borneol and *iso*borneol are geometrical isomerides.

Experimental.

Pure *d*-fenchone was obtained from fennel oil by Gardner and Cockburn's method (J., 1898, **73**, 275); it distilled at 81°/18 mm. and set to a mass of white, prismatic needles at 5—6°: it had $[\alpha]_D^{20°}$ + 62·62° and $D_4^{20°}$ 0·9460. It readily gave an oxime which melted at 168° and possessed the following rotatory powers in 5% solution in benzene: $[\alpha]_{6708}$ + 63·7°, $[\alpha]_{5893}$ + 86·8°, $[\alpha]_{5780}$ + 91·6°, $[\alpha]_{5461}$ + 105·4°, $[\alpha]_{4359}$ + 191·4°.

By the reduction of *d*-fenchone with sodium in boiling ethyl-alcoholic solution, a mixture of α- and β-fenchyl alcohols was obtained containing the components in the proportion of about 9 : 1. The proportion of the β-isomeride was not increased by any of the other methods of reduction which were tried.

α-Fenchyl alcohol was separated from this mixture by the following method. The mixture was heated with phthalic anhydride (1 mol.) at 115—120° for 12 hours, and the product worked up in the usual manner. Previous to any crystallisation, the mixture of fenchyl hydrogen phthalates melted at 136—140° and had

$[\alpha]_D + 19{\cdot}4°$ in 5% ethyl-alcoholic solution. After six recrystallisations from glacial acetic acid, a constant rotatory power and a constant melting point were reached. This pure *d*-fenchyl hydrogen phthalate forms long, prismatic needles which melt at 146° and in 5% solution in ethyl alcohol give the following rotatory powers: $[\alpha]_{5893} + 21{\cdot}6°$, $[\alpha]_{5461} + 27{\cdot}0°$, $[\alpha]_{4359} + 65{\cdot}2°$.

These values were unaltered after the *strychnine* salt of the hydrogen phthalate had been crystallised from ethyl alcohol and subsequently decomposed (Found by titration: *M*, 302·3. Calc., *M*, 302).

It forms a *magnesium* salt which crystallises from aqueous alcohol in needles, m. p. 290—295° (*vide infra*). Hydrolysis of the hydrogen phthalate was effected by heating with aqueous caustic soda and removing the α-fenchyl alcohol in a current of steam.

α-Fenchyl alcohol distils at 94°/20 mm. and crystallises in long, stout prisms, m. p. 47°; it possesses an odour resembling that of camphor and somewhat sweeter than that of *d*-fenchone. The rotatory powers are given in Table I.

α-*Fenchyl* p-*nitrobenzoate*, prepared by the action of *p*-nitrobenzoyl chloride on the alcohol in pyridine solution, crystallises from alcohol or glacial acetic acid in pale yellow needles, m. p. 108—109°. It possesses the following rotatory powers in benzene and carbon disulphide (5% solutions), respectively: $[\alpha]_{6708} -13{\cdot}9°$ and $-16{\cdot}1°$; $[\alpha]_{5893} -17{\cdot}4°$ and $-20{\cdot}0°$; $[\alpha]_{5780} -18{\cdot}0°$ and $-21{\cdot}9°$; $[\alpha]_{5461} -19{\cdot}6°$ and $-23{\cdot}2°$; $[\alpha]_{4359} -29{\cdot}5°$ and $-35{\cdot}4°$.

α-*Fenchyl* p-*chlorobenzoate*, prepared in a similar manner, crystallises from alcohol in needles, m. p. 73—74° (Found by hydrolysis with alcoholic potassium hydroxide; *M*, 293. Calc., *M*, 292).

β-*Fenchyl Alcohol*.—The separation of β-fenchyl hydrogen phthalate from the acetic acid mother-liquors from which the α-fenchyl hydrogen phthalate had been incompletely removed proved to be extremely tedious by the process of fractional precipitation or crystallisation, and after many trials was abandoned. The whole of the hydrogen phthalates were therefore thrown out of solution by addition of water, and portions were converted into salts with different metals. It was hoped that fractional crystallisation of one of these would bring about the separation of the desired β-isomeride. The salt with magnesium appeared to be the most hopeful and the systematic fractional crystallisation of this was resorted to. The result, however, was to bring out as the least soluble fraction a magnesium salt which on decomposition yielded pure α-fenchyl hydrogen phthalate. The hydrogen phthalates were therefore recovered from the more soluble fractions of the magnesium salt and hydrolysed. The impure β-fenchyl alcohol thus obtained

was converted into the *p*-nitrobenzoate, m. p. 80—90°. This mixture of esters after four recrystallisations from glacial acetic acid gave a crop of crystals which melted at 108—109° and corresponded with α-fenchyl *p*-nitrobenzoate. The first two mother-liquors from this series of crystallisations were precipitated with excess of water, when a *p*-nitrobenzoate was obtained of $[\alpha]_D + 7{\cdot}0°$. This was largely the β-isomeride and after some eight crystallisations from ethyl alcohol pure β-fenchyl *p*-nitrobenzoate was obtained as clusters of pale yellow, feathery needles, m. p. 82—83° (Found: N, 4·7. Calc., N, 4·6%).

Specific Rotatory Powers of β-*Fenchyl* p-*Nitrobenzoate.*

Conc.	Solvent.	$[\alpha]_{6708}$.	$[\alpha]_{5893}$.	$[\alpha]_{5780}$.	$[\alpha]_{5461}$.	$[\alpha]_{4359}$.
5%	Benzene	+8·2°	+10·5°	+11·4°	+13·5°	+23·6°
5%	Carbon disulphide	10·3	13·5	14·8	17·7	28·4

This *p*-nitrobenzoate (70 g.) was hydrolysed by heating with alcoholic caustic potash (1 mol.) for ½ hour. β-Fenchyl alcohol distils at 91°/18 mm. and melts at 3—4° and shows $[\alpha]_D - 23{\cdot}28°$. Its odour is similar to that of α-fenchyl alcohol.

β-*Fenchyl hydrogen phthalate*, prepared by the method described above and crystallised twice from acetic acid, forms small, white needles which melt at 153° and give the following rotatory powers in 5% solution in ethyl alcohol: $[\alpha]_{6708} + 7{\cdot}5°$, $[\alpha]_{5893} + 10{\cdot}3°$, $[\alpha]_{5780} + 11{\cdot}3°$, $[\alpha]_{5461} + 13{\cdot}3°$, $[\alpha]_{4359} + 26{\cdot}3°$. On hydrolysis, this ester yielded β-fenchyl alcohol of unchanged rotatory power.

The oxidation of the α-*and* β-*fenchyl alcohols to fenchone* was effected by means of chromic acid mixture and the following results were obtained ($l = 25$ mm.):

	$\alpha_D^{20°}$.
Fenchone from α-fenchyl alcohol,	+14·77°.
,, ,, β- ,, ,,	14·64.
,, ,, original sample	14·81.

Each sample of fenchone was converted into the oxime and by the method of mixed melting-point determination found to be identical with the original *d*-fenchoneoxime of melting point 167—168°.

*l-iso*Borneol was readily obtained by the fractional crystallisation of the cinchonine salts of *dl-iso*bornyl hydrogen phthalate (Part I, *loc. cit.*): these authors used the *l*-menthylamine salt of the hydrogen phthalate for the preparation of *d-iso*borneol, but we have found that the expensive *l*-menthylamine can be replaced with advantage by the more accessible strychnine. The partly active *d-iso*bornyl hydrogen phthalate recovered from the more

soluble portions of the cinchonine salt was dissolved in hot ethyl alcohol, and the calculated amount of strychnine added. After six or seven recrystallisations, the optically pure *l*B, *d*A salt was obtained as fine, glistening needles, m. p. 231—232°.

The rotatory powers of the *d*- and *l*-*iso*borneols are in excellent agreement with those given by the above-mentioned authors.

l-Borneol was prepared from natural borneol ($[\alpha]_D$ 36·0° in 5% ethyl-alcoholic solution) obtained from Schimmel, by crystallisation of the strychnine salt of *l*-bornyl hydrogen phthalate. After four crystallisations from ethyl alcohol, the optically pure *l*B, *l*A salt was obtained as fine crystalline needles, m. p. 202°. The rotatory power of the *l*-borneol thus obtained was identical with that quoted in Part I (*loc. cit.*).

Esters of the normal fatty acids with α- and β-fenchyl alcohols, *d*- and *l*-*iso*borneols and *l*-borneol were prepared by the usual methods. They are, for the most part, pleasant-smelling liquids the physical constants of which are given in the tables.

Table I.

Specific Rotatory Powers of the Esters in the Homogeneous State at 20°.

		λ.				
	$D_4^{20°}$.	6708.	5893.	5780.	5461.	4359.
α-Fenchyl alcohol	0·9641	−9·83°	−12·88°	−13·48°	−15·04°	−26·14°
,, formate	0·9902	57·07	75·36	78·84	89·67	151·98
,, acetate	0·9695	48·34	63·74	66·82	75·73	128·93
,, propionate	0·9614	45·87	60·47	63·30	71·62	121·63
,, *n*-butyrate	0·9522	40·56	53·77	56·00	63·50	107·16
,, *n*-valerate	0·9453	37·07	48·94	51·35	58·03	98·59
,, *n*-hexoate	0·9400	35·70	47·38	49·30	55·98	95·87
,, *n*-heptoate	0·9338	35·30	46·39	48·68	55·13	93·81
,, *n*-octoate	0·9277	33·44	44·09	46·26	52·43	89·10
,, *n*-nonoate	0·9235	30·21	39·85	41·65	47·17	80·35
,, *n*-laurate	0·9160	27·21	36·35	38·25	43·17	74·06
,, *n*-myristate	0·9092	26·62	34·98	36·74	41·57	70·83
β-Fenchyl alcohol	0·9605	17·55	23·28	24·40	27·97	48·37
,, formate	0·9933	8·19	10·93	11·40	12·88	22·59
,, acetate	0·9694	10·61	14·09	14·81	16·90	29·05
,, propionate	0·9601	9·56	12·67	13·31	14·98	25·92
,, *n*-butyrate	0·9531	5·67	7·47	7·95	9·17	15·74
l-Bornyl formate	1·0100	36·62	48·61	50·71	57·60	98·12
,, acetate	0·9920	32·32	42·74	44·56	50·45	85·12
,, propionate	0·9768	30·32	40·03	41·91	47·40	80·08
,, *n*-butyrate	0·9674	28·55	37·44	39·36	44·65	75·24
,, *n*-valerate	0·9574	27·34	35·93	37·35	42·39	71·40
d-*iso*Bornyl formate	1·0136	+22·32	+29·46	+30·55	+34·87	+ 60·03
l- ,, acetate	0·9905	−38·08	−50·18	−52·76	−59·67	−101·00
d- ,, propionate	0·9798	+38·19	+50·21	+52·38	+59·48	+100·19
l- ,, *n*-butyrate	0·9690	−37·41	−49·25	−51·23	−58·15	− 98·59
d- ,, *n*-valerate	0·9592	+36·24	+48·00	+50·46	+56·98	+ 95·98

TABLE II.

Determinations of Rotatory Power in Various Solvents at 20° C. $l = 200$ mm.

Solute.	Solvent.	Grams of solute in 100 c.c. of solution.	α_λ. λ 6708.	5893.	5780.	5461.	4359.	$[\alpha]_\lambda$. λ 6708.	5893.	5780.	5461.	4359.
α-Fenchyl alcohol	Ethyl alcohol	5·01	−0·97°	−1·28°	−1·38°	−1·54°	− 2·71°	− 9·68°	−12·77°	−13·77°	−15·37°	−27·07°
,, ,,	Carbon disulphide	5·00	0·42	0·58	0·61	0·67	1·11	4·20	5·80	6·10	6·70	11·10
,, ,,	Benzene	5·00	0·45	0·62	0·66	0·76	1·38	4·50	6·20	6·60	7·60	13·80
β-Fenchyl alcohol	Ethyl alcohol	4·35	1·48	1·88	2·01	2·28	4·00	17·02	21·62	23·12	26·23	46·01
,, ,,	Carbon disulphide	4·32	2·13	2·76	2·90	3·31	5·97	24·63	31·91	33·53	38·27	69·02
α-Fenchyl formate	Ethyl alcohol	5·00	−5·50	−7·24	−7·64	−8·65	−14·72	−55·00	−72·40	−76·40	−86·50	−147·20
,, acetate	,, ,,	5·10	4·84	6·41	6·72	7·64	13·10	47·45	62·84	65·90	74·90	128·43
,, propionate	,, ,,	5·00	4·41	5·83	6·22	6·98	11·83	44·00	58·23	62·13	69·72	118·16
,, *n*-butyrate	,, ,,	5·02	3·81	5·06	5·34	6·01	10·37	37·95	50·40	53·19	59·86	103·29
,, *n*-valerate	,, ,,	5·03	3·51	4·63	4·95	5·52	9·48	34·89	46·02	49·20	54·87	94·23
,, *n*-hexoate	,, ,,	5·01	3·33	4·43	4·67	5·28	8·98	33·23	44·21	46·61	52·68	89·65
,, *n*-heptoate	,, ,,	5·02	3·30	4·40	4·57	5·17	8·80	32·87	43·82	45·52	51·49	87·65
,, *n*-octoate	,, ,,	5·00	3·05	4·11	4·25	4·83	8·28	30·50	41·10	42·50	48·30	82·80
,, *n*-nonoate	,, ,,	5·00	2·72	3·65	3·79	4·27	7·32	27·17	36·46	37·86	42·66	73·13
,, *n*-laurate	,, ,,	5·01	2·62	3·49	3·59	4·04	6·93	26·15	34·83	35·83	40·32	69·16
,, *n*-myristate	,, ,,	5·02	2·41	3·24	3·31	3·73	6·45	23·98	32·24	32·94	37·11	64·18
,, formate	Carbon disulphide	5·02	−4·68	−6·20	−6·42	−7·28	−12·28	−46·61	−61·75	−63·94	−72·51	−122·3
,, acetate	,, ,,	5·01	3·60	4·74	4·92	5·58	9·25	35·93	47·31	49·10	55·69	92·32
,, propionate	,, ,,	5·00	3·32	4·35	4·50	5·09	8·50	33·20	43·50	45·40	50·90	85·00
,, *n*-butyrate	,, ,,	5·00	2·83	3·85	4·08	4·62	7·70	28·30	38·50	40·80	46·20	77·00
,, *n*-valerate	,, ,,	5·00	2·55	3·44	3·64	4·10	6·84	25·50	34·40	36·40	41·00	68·40
,, *n*-hexoate	,, ,,	5·00	2·44	3·29	3·50	3·98	6·54	24·40	32·90	35·00	39·80	65·40
,, *n*-heptoate	,, ,,	5·00	2·36	3·15	3·36	3·78	6·33	23·60	31·50	33·60	37·80	63·30
,, *n*-octoate	,, ,,	5·00	2·22	2·89	3·10	3·49	5·90	22·18	28·87	30·97	34·87	58·94
,, *n*-nonoate	,, ,,	5·00	1·98	2·61	2·82	3·18	5·37	19·80	26·10	28·20	31·80	53·70
,, *n*-laurate	,, ,,	5·00	1·81	2·48	2·68	3·05	5·04	18·10	24·80	26·80	30·50	50·40
,, *n*-myristate	,, ,,	5·00	1·68	2·25	2·45	2·78	4·64	16·80	22·50	24·50	27·80	46·40
β-Fenchyl formate	Ethyl alcohol	5·03	0·76	0·98	1·05	1·18	2·04	7·56	9·75	10·45	11·74	20·32
,, acetate	,, ,,	5·05	0·82	1·12	1·21	1·40	2·41	8·13	11·10	12·00	13·88	23·89
,, propionate	,, ,,	5·01	0·78	1·00	1·05	1·26	2·12	7·78	9·98	10·48	12·57	21·16
,, *n*-butyrate	,, ,,	4·56	0·42	0·53	0·54	0·60	1·01	4·61	5·81	5·92	6·58	11·08
,, formate	Carbon disulphide	5·04	0·92	1·29	1·38	1·59	2·64	9·14	12·81	13·70	15·79	26·22

β-Fenchyl acetate	Carbon disulphide	5·00	1·00	1·35	1·44	1·67	2·84	9·99	13·49	14·39	16·68	28·37
" propionate	" "	5·00	0·91	1·24	1·32	1·52	2·63	9·10	12·40	13·20	15·20	26·30
" *n*-butyrate	" "	4·33	0·46	0·60	0·67	0·77	1·38	5·31	6·93	7·74	8·89	15·94
l-Borneol	Ethyl alcohol	5·00	2·82	3·71	3·78	4·20	7·40	28·19	37·09	37·79	41·98	73·98
"	Carbon disulphide	5·00	3·18	4·13	4·28	4·88	8·23	31·80	41·30	42·80	48·80	82·30
*l-iso*Borneol	Ethyl alcohol	5·32	2·89	3·68	3·75	4·21	7·16	27·16	34·59	35·25	39·57	67·30
"	Carbon disulphide	5·00	1·92	2·39	2·45	2·72	4·60	19·20	23·98	24·43	27·19	45·99
l-Bornyl formate	Ethyl alcohol	5·10	3·59	4·77	4·83	5·48	9·48	35·18	46·75	47·34	53·70	92·91
" acetate	" "	5·10	3·56	4·72	4·80	5·38	9·24	34·90	46·27	46·96	52·75	90·59
" propionate	" "	5·03	3·24	4·24	4·39	5·02	8·48	32·21	42·15	43·64	49·91	84·31
" *n*-butyrate	" "	5·03	3·06	3·97	4·11	4·62	7·76	30·43	39·48	40·87	45·95	77·16
" *n*-valerate	" "	5·05	2·95	3·59	3·78	4·28	7·32	29·20	35·53	37·41	42·36	72·45
" formate	Carbon disulphide	5·04	3·28	4·35	4·68	5·25	8·92	32·54	43·16	46·43	52·09	88·50
" acetate	" "	5·02	3·03	3·99	4·17	4·71	8·04	30·20	39·76	41·56	46·94	80·13
" propionate	" "	4·98	2·78	3·56	3·74	4·22	7·12	27·91	35·74	37·54	42·36	71·47
" *n*-butyrate	" "	5·07	2·53	3·22	3·44	3·92	6·72	24·93	31·73	33·90	38·63	66·22
" *n*-valerate	" "	5·01	2·46	3·17	3·27	3·72	6·32	24·56	31·65	32·64	37·14	63·10
*d-iso*Bornyl formate	Ethyl alcohol	5·08	+2·42	+3·00	+3·15	+3·59	+ 5·96	+23·83	+29·54	+31·02	+35·35	+ 58·69
l- " acetate	" "	5·04	−4·04	−5·35	−5·57	−6·22	−10·67	−40·10	−53·09	−55·28	−61·73	−105·9
d- " propionate	" "	5·01	+4·12	+5·47	+5·82	+6·51	+10·94	+41·13	+54·61	+58·10	+65·00	+109·2
l- " *n*-butyrate	" "	4·98	−4·02	−5·40	−5·50	−6·24	−10·57	−40·39	−54·25	−55·26	−62·69	−106·2
d- " *n*-valerate	" "	4·97	+4·02	+5·23	+5·38	+6·07	+10·23	+40·26	+52·65	+54·16	+60·12	+104·1
d- " formate	Carbon disulphide	5·02	+2·13	+2·71	+2·87	+3·23	+ 5·32	+21·22	+27·00	+28·59	+32·18	+ 53·00
l- " acetate	" "	5·05	−3·70	−4·73	−4·99	−5·65	− 9·59	−36·62	−46·81	−49·38	−55·91	− 94·91
d- " propionate	" "	5·00	+3·61	+4·66	+4·87	+5·50	+ 9·20	+36·08	+46·57	+48·67	+54·96	+ 91·94
l- " *n*-butyrate	" "	4·99	−3·48	−4·50	−4·63	−5·32	− 8·90	−34·85	−45·06	−46·25	−53·27	− 89·13
d- " *n*-valerate	" "	5·01	+3·41	+4·45	+4·60	+5·25	+ 8·75	+34·03	+44·40	+45·90	+52·38	+ 87·10

Table III.

Photographic Determinations of Rotatory Power in the Homogeneous State at 20°.

"α"-Fenchyl formate.			"β"-Fenchyl alcohol.		
Wave-length. λ.	Obs. rot. power. (l=50 mm.).	Spec. rot. power. $[\alpha]_{\lambda}^{20°}$.	Wave-length. λ.	Obs. rot. power. (l=100 mm.).	Spec. rot. power. $[\alpha]_{\lambda}^{20°}$.
4156 Å.	− 85·00°	−171·68°	4337 Å.	−47·00°	−48·73°
4015 Å.	− 92·00	−185·84	4144 Å.	−53·00	−54·96
3913 Å.	− 99·00	−199·96	3978 Å.	−59·00	−61·18
3800 Å.	−106·00	−214·12	3836 Å.	−65·00	−67·40

Table IV.

Refractive Indices of the "α"-Fenchyl Esters.

Measured in a Pulfrich Refractometer at 20°.

Wave-length.	α-Fenchyl formate.	α-Fenchyl acetate.	α-Fenchyl propionate.	α-Fenchyl *n*-butyrate.	α-Fenchyl *n*-valerate.	α-Fenchyl *n*-hexoate.
6708 Å.	1·4582	1·4541	1·4528	1·4536	1·4551	1·4557
6402	1·4588	1·4549	1·4534	1·4544	1·4558	1·4563
6096	1·4601	1·4561	1·4547	1·4556	1·4570	1·4575
5896	1·4610	1·4570	1·4556	1·4564	1·4579	1·4585
5882	1·4606	1·4567	1·4552	1·4561	1·4576	1·4581
5790	1·4614	1·4573	1·4560	1·4568	1·4583	1·4589
5782	1·4615	1·4574	1·4561	1·4569	1·4584	1·4590
5700	1·4618	1·4577	1·4564	1·4572	1·4587	1·4593
5461	1·4629	1·4588	1·4576	1·4583	1·4598	1·4602
5218	1·4643	1·4602	1·4588	1·4596	1·4612	1·4617
5153	1·4647	1·4607	1·4594	1·4601	1·4616	1·4622
5106	1·4650	1·4610	1·4597	1·4603	1·4620	1·4626
4359	1·4713	1·4671	1·4658	1·4665	1·4681	1·4698
4046	1·4751	1·4710	1·4685	1·4703	1·4718	1·4736

Wave-length.	α-Fenchyl *n*-heptoate.	α-Fenchyl *n*-octoate.	α-Fenchyl *n*-nonoate.	α-Fenchyl laurate.	α-Fenchyl myristate.
6708 Å.	1·4563	1·4569	1·4576	1·4590	1·4608
6402	1·4570	1·4576	1·4583	1·4598	1·4613
6096	1·4582	1·4589	1·4596	1·4610	1·4626
5896	1·4591	1·4596	1·4603	1·4619	1·4635
5882	1·4588	1·4593	1·4604	1·4615	1·4630
5790	1·4595	1·4600	1·4606	1·4623	1·4638
5782	1·4596	1·4601	1·4607	1·4623	1·4637
5700	1·4598	1·4604	1·4601	1·4626	1·4642
5461	1·4610	1·4615	1·4621	1·4638	1·4654
5218	1·4624	1·4629	1·4635	1·4651	1·4666
5153	1·4628	1·4633	1·4640	1·4655	1·4671
5106	1·4632	1·4637	1·4644	1·4658	1·4674
4359	1·4694	1·4700	1·4704	1·4721	1·4738
4046	1·4732	—	—	1·4759	1·4777

TABLE IV *continued.*

Refractive Indices of the " β *"-Fenchyl Esters at* 20°.

Wave-length.	β-Fenchyl formate.	β-Fenchyl acetate.	β-Fenchyl propionate.	β-Fenchyl *n*-butyrate (at 17·5°).
6708 Å.	1·4594	1·4556	1·4543	1·4553
6402	1·4601	1·4563	1·4550	1·4561
6096	1·4613	1·4576	1·4562	1·4572
5896	1·4623	1·4584	1·4571	1·4580
5882	1·4619	1·4581	1·4568	1·4578
5790	1·4625	1·4588	1·4574	1·4585
5782	1·4625	1·4589	1·4575	1·4586
5700	1·4629	1·4591	1·4577	1·4589
5461	1·4640	1·4601	1·4589	1·4601
5218	1·4654	1·4616	1·4602	1·4613
5153	1·4658	1·4620	1·4607	1·4617
5106	1·4661	1·4624	1·4610	1·4621
4359	1·4724	1·4697	1·4672	1·4684
4046	1·4762	1·4735	1·4710	—

Refractive Indices of Bornyl and iso*Bornyl Esters at* 20°.

Ester.	Wave-length in Å. 6708.	5896.	5790.	5461.	4359.
l-Bornyl formate	1·4661	1·4689	1·4693	1·4710	1·4795
" acetate	1·4607	1·4634	1·4640	1·4656	1·4740
" propionate	1·4583	1·4612	1·4617	1·4632	1·4715
" *n*-butyrate	1·4584	1·4613	1·4618	1·4633	1·4716
" *n*-valerate	1·4586	1·4615	1·4620	1·4635	1·4718
*d-iso*Bornyl formate	1·4678	1·4707	1·4712	1·4728	1·4814
l- " acetate	1·4606	1·4633	1·4639	1·4655	1·4738
d- " propionate	1·4590	1·4619	1·4624	1·4639	1·4723
l- " *n*-butyrate	1·4594	1·4623	1·4628	1·4643	1·4727
d- " *n*-valerate	1·4596	1·4625	1·4630	1·4645	1·4729

TABLE V.

Observations of Density ($D_4^{t°}$) *and of Rotatory Power* ($\alpha_{50\ mm.}$) *of the Compounds in the Homogeneous State.*

(The densities were determined in a pyknometer of about 1·5 c.c. capacity.)

"α"-*Fenchyl alcohol,* b. p. 86°/14 mm.

All rotatory powers are negative.

$D_4^{t°}$ 0·9226 at 62·5°, 0·9034 at 84°, 0·8817 at 103°, 0·8638 at 122°.
α_{6708} 4·31° at 59°, 4·20° at 75°, 4·23° at 92°, 4·38° at 113°, 4·47° at 125°.
α_{5893} 5·77° at 58°, 5·66° at 75°, 5·55° at 92°, 5·74° at 113°, 5·85° at 125°.
α_{5780} 6·11° at 57°, 5·95° at 75°, 5·97° at 92°, 6·07° at 113°, 6·24° at 125°.
α_{5461} 6·83° at 57°, 6·74° at 75°, 6·75° at 92°, 6·87° at 113°, 7·10° at 125°.
α_{4359} 12·01° at 57°, 11·81° at 75°, 11·90° at 92°, 11·95° at 113°, 12·28° at 125°.

"β"-*Fenchyl alcohol,* b. p. 83°/12 mm.

$D_4^{t°}$ 0·9625 at 18°, 0·9333 at 50°, 0·8999 at 83·5°, 0·8618 at 124°.
α_{6768} 8·40° at 19°, 8·88° at 51°, 8·95° at 80°, 8·72° at 103°, 8·64° at 122°.
α_{5893} 11·13° at 19°, 11·63° at 51°, 11·72° at 80°, 11·41° at 103°, 11·32° at 122°.
α_{5780} 11·71° at 19°, 11·98° at 51°, 12·33° at 80°, 12·09° at 103°, 11·89° at 122°.
α_{5461} 13·41° at 19°, 13·59° at 51°, 13·96° at 80°, 13·68° at 103°, 13·45° at 122°.
α_{4359} 23·18° at 19°, 23·91° at 51°, 24·08° at 80°, 23·57° at 103°, 23·07° at 122°.

TABLE V (*continued*).

"α"-*Fenchyl formate*, b. p. 97°/21 mm.

$D_{4^\circ}^{t^\circ}$ 0·9929 at 17°, 0·9568 at 59°, 0·9275 at 91°, 0·9076 at 114°.
α_{6708} 28·26° at 20°, 25·82° at 45°, 23·36° at 74°, 21·37° at 102·5°, 20·18° at 123°.
α_{5893} 37·31° at 20°, 34·27° at 45°, 31·04° at 74°, 28·36° at 102·5°, 26·65° at 123°.
α_{5780} 39·03° at 20°, 35·88° at 45°, 32·44° at 74°, 29·88° at 102·5°, 28·01° at 123°.
α_{5461} 44·39° at 20°, 40·87° at 45°, 36·94° at 74°, 33·97° at 102·5°, 31·71° at 123°.
α_{4359} 75·23° at 20°, 69·23° at 45°, 62·99° at 74°, 57·89° at 102·5°, 53·79° at 123°.

"α"-*Fenchyl acetate*, b. p. 99°/19 mm.

$D_{4^\circ}^{t^\circ}$ 0·9725 at 17°, 0·9326 at 61·5°, 0·9041 at 92°, 0·8827 at 114°.
α_{6708} 28·82° at 14°, 21·42° at 52·5°, 19·44° at 87·5°, 18·54° at 102°, 17·23° at 129°.
α_{5893} 31·41° at 14°, 28·25° at 52·5°, 25·63° at 87°, 24·43° at 102·5°, 22·71° at 129°.
α_{5780} 32·95° at 14°, 29·49° at 52·5°, 26·77° at 87·5°, 25·72° at 102·5°, 23·87° at 129°.
α_{5461} 37·36° at 14°, 33·42° at 52·5°, 30·21° at 87·5°, 28·94° at 103°, 26·95° at 130°.
α_{4359} 63·60° at 14°, 56·90° at 52·5°, 51·65° at 87°, 49·17° at 102·5°, 45·66° at 128·5°.

"α"-*Fenchyl propionate*, b. p. 115°/21 mm.

$D_{4^\circ}^{t^\circ}$ 0·9565 at 14°, 0·9302 at 56°, 0·9080 at 83°, 0·8802 at 111°.
α_{6708} 22·05° at 20°, 20·04° at 47·5°, 18·60° at 73°, 17·40° at 95·5°, 16·25° at 120°.
α_{5893} 29·07° at 20°, 26·42° at 47·5°, 24·57° at 73°, 23·00° at 95·5°, 21·47° at 120°.
α_{5780} 30·43° at 20°, 27·61° at 47·5°, 25·85° at 73°, 23·95° at 95·5°, 22·32° at 120°.
α_{5461} 34·43° at 20°, 31·35° at 47·5°, 29·34° at 73°, 27·21° at 95·5°, 25·23° at 120°.
α_{4359} 58·47° at 20°, 52·82° at 47·5°, 49·34° at 73°, 45·95° at 95°, 42·88° at 120°.

"α"-*Fenchyl* n-*butyrate*, b. p. 127°/21 mm.

$D_{4^\circ}^{t^\circ}$ 0·9607 at 10°, 0·9279 at 48°, 0·9072 at 73·5°, 0·8736 at 111°.
α_{6708} 19·31° at 20°, 17·54° at 52°, 15·88° at 87°, 15·20° at 103°, 14·27° at 123°.
α_{5893} 25·60° at 20°, 23·15° at 52°, 20·88° at 87°, 20·04° at 103°, 18·81° at 123°.
α_{5780} 26·66° at 20°, 24·16° at 52°, 21·78° at 87°, 20·90° at 103°, 19·75° at 123°.
α_{5461} 30·23° at 20°, 27·44° at 52°, 24·69° at 87°, 23·66° at 103°, 22·22° at 123°.
α_{4359} 51·02° at 20°, 46·78° at 52°, 42·45° at 87°, 40·14° at 103°, 37·83° at 123°.

"α"-*Fenchyl* n-*valerate*, b. p. 135°/15 mm.

$D_{4^\circ}^{t^\circ}$ 0·9517 at 12·5°, 0·9141 at 57°, 0·8948 at 81°, 0·8754 at 103°.
α_{6708} 17·56° at 19°, 16·37° at 46·5°, 14·83° at 80°, 13·93° at 103°, 13·00° at 125°.
α_{5893} 23·19° at 19°, 21·67° at 46·5°, 19·60° at 80°, 18·40° at 103°, 17·11° at 125°.
α_{5780} 24·32° at 19°, 22·77° at 46·5°, 21·03° at 80°, 19·52° at 103°, 18·26° at 125°.
α_{5461} 27·48° at 19°, 25·79° at 46·5°, 23·59° at 80°, 21·87° at 103°, 20·51° at 125°.
α_{4359} 46·72° at 19°, 43·62° at 46·5°, 39·28° at 80°, 36·57° at 103°, 34·42° at 125°.

TABLE V (*continued*).

"α"-*Fenchyl* n-*hexoate*, b. p. 152°/17 mm.

$D_4^{t°}$	0·9471 at 11·5°, 0·9194 at 45°, 0·8983 at 69°, 0·8632 at 112°.
a_{6708}	16·78° at 20°, 15·45° at 49°, 14·02° at 81°, 13·03° at 103°, 12·03° at 123°.
a_{5893}	22·27° at 20°, 20·64° at 49°, 18·63° at 81°, 17·40° at 103°, 16·32° at 123°.
a_{5780}	23·17° at 20°, 21·47° at 48°, 19·56° at 81°, 18·27° at 103°, 17·12° at 123°.
a_{5461}	26·31° at 20°, 24·35° at 48°, 22·09° at 81°, 20·77° at 103°, 19·24° at 123°.
a_{4359}	45·06° at 20°, 41·40° at 49°, 37·56° at 81°, 34·85° at 103°, 32·50° at 123°.

"α"-*Fenchyl* n-*heptoate*, b. p. 160°/16 mm.

$D_4^{t°}$	0·9428 at 8·5°, 0·9097 at 50°, 0·8868 at 79°, 0·8630 at 107°.
a_{6708}	16·69° at 16°, 14·76° at 53·5°, 13·15° at 93°, 12·17° at 121°.
a_{5893}	22·00° at 16°, 19·41° at 53·5°, 17·10° at 95°, 15·83° at 121°.
a_{5780}	23·03° at 16°, 20·33° at 53·5°, 18·11° at 94°, 16·58° at 122°.
a_{5461}	26·04° at 16°, 23·09° at 53·5°, 20·53° at 92°, 18·81° at 122°.
a_{4359}	44·34° at 16°, 39·29° at 54°, 34·55° at 93·5°, 31·75° at 123°.

"α"-*Fenchyl* n-*octoate*, b. p. 176°/25 mm.

$D_4^{t°}$	0·9332 at 13·5°, 0·8941 at 63°, 0·8770 at 83°, 0·8539 at 113°.
a_{6708}	15·60° at 18°, 14·29° at 48°, 13·20° at 74°, 11·89° at 107°, 11·11° at 130°.
a_{5893}	20·57° at 18°, 18·76° at 49°, 17·40° at 74°, 15·76° at 107°, 14·70° at 130°.
a_{5780}	21·57° at 18°, 19·75° at 47°, 18·44° at 74°, 16·69° at 107°, 15·47° at 130°.
a_{5461}	24·44° at 18°, 22·36° at 47°, 20·70° at 74°, 18·65° at 107°, 17·39° at 130°.
a_{4359}	41·55° at 18°, 37·94° at 48°, 34·76° at 74°, 30·81° at 107°, 28·15° at 130°.

"α"-*Fenchyl* n-*nonoate*, b. p. 185°/16 mm.

$D_4^{t°}$	0·9287 at 13°, 0·8999 at 50·5°, 0·8788 at 78°, 0·8478 at 116°.
a_{6708}	14·18° at 15°, 12·51° at 52·5°, 11·02° at 91°, 10·12° at 113°, 9·73° at 132°.
a_{5893}	18·68° at 15°, 16·46° at 52·5°, 14·44° at 91°, 13·30° at 113°, 12·57° at 132°.
a_{5780}	19·54° at 15°, 17·27° at 52·5°, 15·22° at 91°, 14·10° at 113°, 13·42° at 132°.
a_{5461}	22·09° at 15°, 19·53° at 52·5°, 17·17° at 91°, 15·92° at 113°, 15·12° at 132°.
a_{4359}	37·65° at 15°, 33·40° at 52·5°, 29·79° at 91°, 27·62° at 113°, 26·21° at 132°.

"α"-*Fenchyl laurate*, b. p. 207—209°/14 mm.

$D_4^{t°}$	0·9188 at 15·5°, 0·8906 at 53°, 0·8714 at 78·5°, 0·8466 at 110°.
a_{6708}	12·73° at 12°, 11·41° at 50°, 10·83° at 77°, 10·25° at 98°, 9·39° at 119·5°.
a_{5893}	17·05° at 12°, 15·09° at 50°, 13·93° at 77°, 13·30° at 97°, 12·48° at 119·5°.
a_{5780}	17·91° at 12°, 15·96° at 50°, 14·58° at 77°, 13·92° at 98°, 12·91° at 121°.
a_{5461}	20·24° at 12°, 18·02° at 50°, 16·49° at 77°, 15·68° at 99°, 14·56° at 121·5°.
a_{4359}	34·75° at 12°, 31·03° at 50°, 28·52° at 77°, 26·72° at 98°, 25·15° at 118°.

"α"-*Fenchyl myristate*, b. p. 190—195°/2 mm.

$D_4^{t°}$	0·9121 at 16°, 0·8849 at 53°, 0·8630 at 82°, 0·8453 at 105°.
a_{6708}	12·14° at 19·5°, 10·73° at 60°, 9·53° at 87·5°, 9·17° at 104·5°, 8·57° at 127°.
a_{5893}	15·93° at 19·5°, 13·88° at 60°, 12·62° at 86·5°, 11·92° at 104·5°, 11·12° at 128°.
a_{5780}	16·67° at 20·5°, 14·58° at 59°, 13·43° at 86°, 12·80° at 104°, 11·74° at 127°.
a_{5461}	18·71° at 22·5°, 16·56° at 59°, 15·15° at 86·5°, 14·48° at 104°, 13·35° at 127·5°.
a_{4359}	32·27° at 19·5°, 28·16° at 60°, 25·86° at 86·5°, 24·36° at 107°, 22·87° at 127·5°.

TABLE V (*continued*).

"β"-*Fenchyl formate*, b. p. 83·5°/11 mm.

$D^{t°}_{4°}$ 0·9945 at 18·5°, 0·9634 at 52·5°, 0·9363 at 82·5°, 0·9016 at 118°.
α_{6708} 4·05° at 19·5°, 3·74° at 51·5°, 3·53° at 74°, 3·25° at 96°, 3·06° at 117°.
α_{5893} 5·44° at 19·5°, 4·91° at 51·5°, 4·59° at 74°, 4·29° at 95°, 4·03° at 117°.
α_{5780} 5·67° at 19·5°, 5·02° at 51·5°, 4·75° at 74·5°, 4·43° at 95°, 4·19° at 116·5°.
α_{5461} 6·41° at 19·5°, 5·71° at 51·5°, 5·31° at 74·5°, 4·98° at 95°, 4·67° at 116·5°.
α_{4359} 11·23° at 19·5°, 10·15° at 51·5°, 9·39° at 74·5°, 8·89° at 94°, 8·35° at 116°.

"β"-*Fenchyl acetate*, b. p. 90°/12 mm.

$D^{t°}_{4°}$ 0·9739 at 15°, 0·9397 at 53·5°, 0·9162 at 81°, 0·8906 at 110°.
α_{6708} 5·17° at 18·5°, 4·90° at 49°, 4·48° at 76°, 4·13° at 97°, 3·89° at 114·5°.
α_{5893} 6·85° at 18·5°, 6·38° at 49·5°, 5·88° at 75°, 5·50° at 97°, 5·16° at 114·5°.
α_{5780} 7·25° at 18·5°, 6·57° at 49°, 5·88° at 74°, 5·80° at 97·5°, 5·35° at 114·5°.
α_{5461} 8·23° at 18·5°, 7·48° at 49°, 6·75° at 74°, 6·51° at 97·5°, 6·03° at 114·5°.
α_{4359} 14·14° at 18·5°, 12·95° at 49·5°, 11·87° at 75°, 11·35° at 97°, 10·55° at 114·5°.

"β"-*Fenchyl propionate*, b. p. 102°/11 mm.

$D^{t°}_{4°}$ 0·9614 at 18·5°, 0·9334 at 52°, 0·9059 at 81·5°.
α_{6708} 4·61° at 18°, 4·25° at 44°, 3·95° at 74°, 3·64° at 102°, 3·32° at 125°.
α_{5893} 6·11° at 18°, 5·67° at 44°, 5·16° at 73·5°, 4·70° at 102°, 4·21° at 125°.
α_{5780} 6·42° at 18°, 6·04° at 44°, 5·43° at 74°, 5·08° at 102°, 4·53° at 126·5°.
α_{5461} 7·22° at 18°, 6·74° at 44·5°, 6·04° at 74°, 5·61° at 102·5°, 4·98° at 128°.
α_{4359} 12·51° at 18°, 11·69° at 43·5°, 10·62° at 75·5°, 9·70° at 102·5°, 8·89° at 125°.

"β"-*Fenchyl* n-*butyrate*, b. p. 112°/16 mm., $D^{20°}_{4°}$ 0·9531.

	λ.				
	6708.	5896.	5780.	5461.	4359.
$a^{20°}_{\lambda}$	−2·70°	−3·56°	−3·79°	−4·37°	−7·50°

Esters of l-*Borneol.* $\alpha^{20°}_{\lambda}$ (*l*=50 *mm.*).

		B. p. Mm.	λ. 6708.	5893.	5780.	5461.	4359.
l-Borny	formate	94°/14	−18·49°	−24·55°	−25·61°	−29·09°	−49·55°
,,	acetate	103°/14	16·03	21·15	22·10	25·02	42·22
,,	propionate	114°/12	14·81	19·55	20·47	23·15	39·11
,,	*n*-butyrate	125°/15	13·81	18·11	19·04	21·60	36·39
,,	*n*-valerate	136°/12	13·09	17·20	17·88	20·29	34·18

Esters of iso*Borneol.* $\alpha^{20°}_{\lambda}$ (*l*=50 *mm.*).

		B. p. Mm.	λ. 6708.	5893.	5780.	5461.	4359.
*d-iso*Bornyl	formate	94°/15	−11·31°	−14·93°	−15·48°	−17·63°	−30·42°
l- ,,	acetate	112°/17	18·86	24·85	26·13	29·55	50·02
d- ,,	propionate	119°/16	18·71	24·60	25·66	29·14	49·08
l- ,,	*n*-butyrate	125°/14	18·08	23·86	24·82	28·17	47·76
d- ,,	*n*-valerate	138°/14	17·38	23·02	24·20	27·33	46·03

The authors with to express their indebtedness to the Government Grant Committee of the Royal Society for a grant with the

aid of which some of the materials used in this investigation were purchased, and also to the Department of Scientific and Industrial Research for a grant which enabled one of them (H. E. M. P.) to participate in the work.

BATTERSEA POLYTECHNIC, S.W. 11. [*Received, April 6th*, 1925.]

NOTES.

The Atomic Volume of Manganese. By ALAN N. CAMPBELL.

THE curve of atomic volumes, plotted by means of the usually accepted values of the densities, shows in the neighbourhood of manganese two minima, one at manganese and the other at cobalt, with iron occupying a maximum between. With the new value for the density of manganese (Campbell, J., 1923, **123**, 2323), the two minima persist, but the first minimum is shifted from manganese to chromium.

	V.	Cr.	Mn.	Fe.	Ni.	Co.	Cu.
At. wts.....	51·0	52·0	54·9	55·8	58·7	59·0	63·6
At. vols.	9·26	7·55	7·34 (old value) 7·76 (new value)	7·46	6·65	6·59	7·1

If the accepted value of the density of chromium should prove to be too high, the atomic volume of chromium would probably cease to be a minimum, and only one minimum would exist at cobalt, as is the case in all the other loops of the atomic-volume curve. —[*Received, March 30th*, 1925.]

Molybdenum Pentoxide. By WILLIAM WARDLAW and FRANK HAROLD NICHOLLS.

VARIOUS oxides intermediate between the dioxide and trioxide of molybdenum have been described. These substances, such as Mo_4O_{11}, Mo_3O_8, and Mo_5O_{12}, were investigated by Guichard (*Compt. rend.*, 1899, **129**, 722), who, finding that in every case sufficient purification with ammonia and hydrochloric acid left molybdenum dioxide, concluded that no homogeneous oxide between MoO_2 and MoO_3 exists. On the other hand, Smith and Oberholtzer (*Z. anorg.*

Chem., 1893, **4**, 236), by prolonged heating of the trioxide at 105—120° in dry hydrogen iodide, obtained a violet-blue product, $Mo_2O_5,1{\cdot}5H_2O$, which was stable in air but was completely dehydrated at a red heat, yielding a brown substance, Mo_2O_5. Again, the hydroxide, $MoO(OH)_3$, obtained by the action of ammonia on ammonium molybdenyl chloride, $MoOCl_3,2NH_4Cl$ (Klason, *Ber.*, 1901, **31**, 148), leaves, when cautiously heated in a stream of carbon dioxide, a violet-black powder which is soluble in sulphuric and hydrochloric acids with a difficulty varying with its temperature of preparation. It has the formula Mo_2O_5 and, according to Klason, is but slightly contaminated with trioxide and dioxide. So-called alkali salts of molybdenum pentoxide, $(NH_4)Mo_2O_5,3H_2O$, $NaMo_2O_5,3H_2O$, $BaMo_2O_5,3H_2O$, have been described by Mawrow and Nikolow (*Z. anorg. Chem.*, 1915, **92**, 138). It is difficult to see how these compounds can be regarded as derivatives of Mo_2O_5.

Pure molybdenum pentoxide is readily prepared by carefully heating the oxysulphate (J., 1924, **125**, 1910) or the oxyoxalate (this vol., p. 1311) of tervalent molybdenum in a current of nitrogen:

$$Mo_2O(SO_4)_2 = Mo_2O_5 + 2SO_2. \quad Mo_2O(C_2O_4)_2 = Mo_2O_5 + 4CO.$$

The molybdenum content of the violet-black residue was determined by dissolving a weighed quantity in acid, precipitating the molybdenum as sulphide, and igniting to the trioxide (Found: Mo, 70·4. Mo_2O_5 requires Mo, 70·6%).

The pentoxide remained almost unchanged (Found: Mo, 70·4%) after being boiled with five successive portions of ammonium hydroxide, washed with distilled water, and dried at 110°; were Guichard's conclusion correct, the product should have been more or less pure molybdenum dioxide. That the ammonia was not without action, however, was proved by the formation of molybdenum-blue when the ammoniacal extract was acidified and treated with hydrogen sulphide.

Like Klason's product, the pentoxide is difficultly soluble in hydrochloric and sulphuric acids.—UNIVERSITY OF BIRMINGHAM. [*Received, March 31st*, 1925.]

Chlorobenzthiazole Dibromide. By ROBERT FERGUS HUNTER.

Two grams of 1-chlorobenzthiazole (prepared according to Hofmann, *Ber.*, 1879, **12**, 1126, with the modification that the phenylthiocarbimide and phosphorus pentachloride were heated under reflux at 160—170° instead of in a sealed tube) were dissolved in 10 c.c. of chloroform and slowly treated with 2 c.c. of bromine. The solution, on being concentrated and cooled, furnished orange-red

needles of a *dibromide*, m. p. 139° after showing a colour change at 130° (Found : Br, 48·8. $C_7H_4NClBr_2S$ requires Br, 48·5%).

The dibromide, which appears to be stable in a vacuum, loses bromine on exposure to air or on treatment with sulphurous acid, with regeneration of the chlorobenzthiazole. The bromine atoms therefore appear to be attached to the nitrogen atom.

Attempts to obtain 1 : 1-bisbenzthiazole (*Ber.*, 1880, **13**, 1223) by the action of sodium upon 1-chlorobenzthiazole in boiling ether or boiling xylene were unsuccessful.—IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY, LONDON, S.W.7. [*Received, April 20th*, 1925.]

A Laboratory Method of Preparing p-*Benzoquinone.* By REGINALD CRAVEN and WILLIAM ALEXANDER TURNER DUNCAN.

PURE *p*-benzoquinone, in quantities of 30—40 g., can be prepared in about 4 hours by the following method : To a mechanically stirred, ice-cold solution of quinol (66 g.) in 300 c.c. of 60% acetic acid, 200 c.c. of 30% acetic acid containing 84 g. of chromic anhydride are added during 2—3 hours, care being taken that the temperature does not exceed 10°. The liquid is filtered at once and the quinone washed several times with a little ice-cold water; m. p. 114·5°.—ROBERT GORDON'S COLLEGES, ABERDEEN. [*Received, April 30th*, 1925.]

Reduction of the Bromoanthraquinones. By EDWARD DE BARRY BARNETT and JAMES WILFRED COOK.

THE chloroanthraquinones on reduction with zinc dust and ammonia pass easily into the corresponding chloroanthracenes, loss of chlorine only taking place in the case of 1 : 2 : 3 : 4-tetrachloroanthraquinone, which gives 2 : 3-dichloroanthracene. Attempts to prepare 1- and 2-bromo- and 2 : 3-dibromo-anthracene by the reduction of the corresponding quinones have shown that in each case bromine is lost, the sole product isolated being anthracene. This reaction is remarkable in view of the non-reactive nature of the bromine atoms in the bromoanthraquinones, and in the very few *Bz*-bromoanthracenes, such as the 2 : 3 : 9 : 10-tetrabromo-compound, which are known.

The 2 : 3-dibromoanthraquinone used in the above experiments was prepared from 9 : 10-dibromoanthracene tetrabromide by the action of alcoholic potassium hydroxide and subsequent oxidation by chromic acid of the resulting 2 : 3 : 9 : 10-tetrabromoanthracene (m. p. 274° : K. H. Meyer and Zahn, *Annalen*, 1913, **396**, 174, give 265—266°). The dibromoanthraquinone melted at 283°,

in agreement with the figure given by Battegay and Claudin (*Bull. Soc. Ind. Mulhouse*, 1920, **86**, 632; *Bull. Soc. chim.*, 1921, **29**, 1017) and Grandmougin (*Compt. rend.*, 1921, **173**, 839), who synthesised it by another method, whereas K. H. Meyer and Zahn (*loc. cit.*) give 269—270°.

9 : 10-Dibromoanthracene tetrabromide when suspended in cold pyridine loses both bromine and hydrogen bromide, and the resulting 2 : 9 : 10-tribromo- and 2 : 3 : 9 : 10-tetrabromo-anthracene can be separated by fractional crystallisation from amyl alcohol.—The Sir John Cass Technical Institute, Jewry Street, Aldgate, London. [*Received, May 14th*, 1925.]

The Reduction of Anethole Nitrosochloride by Stannous Chloride and Hydrochloric Acid. By John Baldwin Shoesmith and Robert Henry Slater.

Twenty grams of anethole nitrosochloride (see Orndorff and Morton, *Amer. Chem. J.*, 1900, **23**, 181) in 150 c.c. of chloroform (the only solvent in which the nitrosochloride is appreciably soluble) were vigorously stirred with 150 g. of stannous chloride dissolved in 200 c.c. of concentrated hydrochloric acid. The emulsion became transparent and yellow whilst its temperature gradually rose to 50°. After ½ hour's stirring, a yellow solid was precipitated and after 6 hours, precipitation was complete, the temperature of the mixture being that of the room. After filtration, the solid was dried over calcium chloride and potassium hydroxide, and unchanged nitrosochloride extracted with chloroform. The residue (m. p. 259° with decomp.) was the double compound of *anisylideneazine hydrochloride* and *stannic chloride*, $(MeO\cdot C_6H_4\cdot CH{:}N\cdot N{:}CH\cdot C_6H_4\cdot OMe,HCl)_2,SnCl_4$ (Found : Cl, 24·7; Sn, 13·1. $C_{32}H_{34}O_4N_4Cl_6Sn$ requires Cl, 24·45; Sn, 13·6%), which with water was decomposed into stannic oxide and anisylideneazine, m. p. 168° (to a liquid crystal which was converted into the isotropic liquid at 180°) (Found : N, 10·8. Calc., N, 10·45%). Anisylideneazine acts as a mono-acid base, and in solution in chloroform is converted by hydrogen chloride into *anisylideneazine hydrochloride*, $MeO\cdot C_6H_4\cdot CH{:}N\cdot N{:}CH\cdot C_6H_4\cdot OMe,HCl$, fine, yellow needles, m. p. 172°, which decompose at 177° (Found : Cl, 11·7. $C_{16}H_{17}O_2N_2Cl$ requires Cl, 11·6%) and give anisaldehyde with nitrous acid and the above double compound with stannic chloride.

The authors wish to acknowledge a grant from the Earl of Moray Research Fund which rendered the investigation possible.—Edinburgh University. [*Received, March 4th*, 1925.]

Oxidations in Turpentine and Olive Oil. By ERNEST WALKER.

A SIMPLE and useful method for the oxidation of organic compounds has been based on the property of turpentine of acquiring oxidising power by exposure to the air for some time. For example, diphenylchloroarsine, or diphenylarsenious oxide, was dissolved in a slight excess of turpentine (which had been thus exposed), and a trace of water added to promote hydrolysis. After a few hours, diphenylarsinic acid separated, m. p. 172° (after recrystallisation from water). In a similar manner, but without the addition of water, ββ′-dichlorodiethyl sulphide was converted into ββ′-dichlorodiethyl sulphoxide, m. p. 109° (after crystallisation from alcohol). Freshly distilled turpentine is quite inactive, but gradually acquires oxidising properties on standing.

Another medium which effects precisely similar oxidations is rancid olive oil. An old specimen of olive oil which has been much exposed to the air is usually sufficiently rancid for the purpose. Otherwise, fresh olive oil can be made rancid by bubbling air through it at about 70° for 24 hours. It is not sufficient for the olive oil simply to contain free fatty acid. Decomposition of the oil must be avoided and the correct degree of rancidity may be gauged by the change in colour of the oil from yellow to a pale green or almost colourless hue. The oil may then be said to be "activated." There can be little doubt that its oxidising properties are due to the presence of peroxides, analogous to those found in exposed turpentine, and that the decoloration of the oil represents the oxidising action of such peroxides upon the pigment present. The products obtained by means of this reagent and by means of turpentine differ only in crystalline form. All three of the preceding substances were oxidised in a similar manner by rancid olive oil. The two arsenic compounds (which are solids) were dissolved in chloroform, and an equal volume of "activated" olive oil was added; in each case diphenylarsinic acid crystallised on standing. In the case of ββ′-dichlorodiethyl sulphide it was found possible greatly to accelerate the oxidation by bubbling air through the solution in the olive oil at 70°. The sulphoxide then commenced to crystallise in the course of a few minutes.—DEPARTMENT OF BIOCHEMISTRY, OXFORD. [*Received, May 11th,* 1925.]

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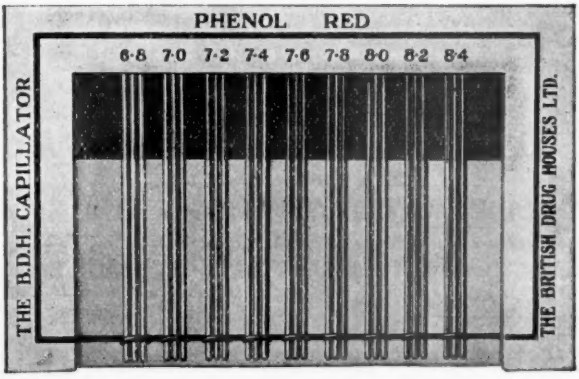

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